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Electrostatic Spray Deposition of Highly Transparent Silver Nanowire Electrode on Flexible Substrate

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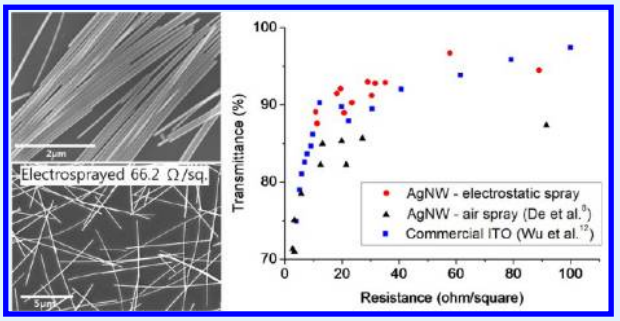
ABSTRACT: In this work, a modified polyol synthesis by adding KBr and by replacing the AgCl with NaCl seed was used to obtain high quality silver nanowires with long aspect ratios with an average length of 13.5 μm in length and 62.5 nm in diameter. The Ag nanowires suspended in methanol solution after removing any unwanted particles using a glass filter system were then deposited on a flexible polycarbonate substrate using an electrostatic spray system. Transmittance of 92.1% at wavelength of 550 nm with sheet resistance of 20 Ω/sq and haze of 4.9% were measured for the electrostatic sprayed Ag nanowire transparent electrode.



KEYWORDS: *transparent electrode, silver, nanowire, polyol, electrostatic spray, flexible substrate*

INTRODUCTION

With advances in current technological developments in displays and solar cells, there is an ever increasing demand for low-cost transparent electrode materials. The most widely used transparent electrode material is indium tin oxide (ITO) owing to its high optical transparency and low sheet resistance,[1−3] but ITO is not able to meet the current and future demands for transparent electrodes in many different applications including displays and solar cells owing to the scarcity and high cost of indium. In addition, ITO is unsuitable for flexible displays and electronics because of the intrinsic brittleness that will result in a brittle fracture after 1% strain[4,5] as well as the high processing temperatures for deposition that may be unsuitable for flexible polymer materials. Therefore, there is a need to develop a new material to replace ITO for future flexible display, electronics, and solar cell applications.

Promising candidates for replacing ITO for flexible transparent electrode applications include metal nanowires, single-walled carbon nanotubes (CNT), and graphenes. Among these candidates, metal nanowires are especially promising due to the higher conductivity of metal compared to the carbon-based CNTs and graphenes. Silver has one of the highest conductivities among different metal choices (Ag = 6.3×10^7 $S \cdot m^{-1}$),[6] and several previous studies have indicated that a transparent electrode with sheet resistance R_s < 100 Ω/sq can easily be achieved from solution-synthesized nanowires and Ag gratings.[7−11] In comparison, solution-dispersed graphene flakes and CNTs were reported at best to have sheet resistance of 200 Ω/sq at an average transmittance of 59%,[12] and 160 Ω/sq at an average transmittance of 87%,[13] respectively. The first demonstration of the Ag nanowire electrode was in the work by Lee et al.,[7] where the solution dispersed Ag nanowires from the polyol reduction method developed by Sun et al.[14] were simply drop-casted onto a glass substrate. The work by Lee et al.[7] demonstrated that the Ag nanowire electrode can result in comparable electrical and optical performance to that of ITO that is able to overcome the limitations of ITO mentioned above including the mechanical brittleness. In addition, the fact that the nanowire electrode could be created from a simple drop casting method has opened up possibilities in using highly scalable processing methodologies to significantly reduce the processing costs compared to those used for ITO. More recently, there is interest in development of large-scale coating processes such as Meyer rod[9,15] or air spray[16] coatings to facilitate a low-cost, uniform coverage over a large area. The air spray deposition of Ag nanowires was demonstrated by De et al.,[8] where an extensive study of optimization parameters to achieve uniform coating using an air spray was reported.

The major drawback of the revolutionary Ag nanowire transparent electrode technology, however, is the fact that the nanowires cause a significant amount of light scattering, where the difference in the total (diffusive) and the specular transmittance was reported to be in the range of 12−18% for a Ag nanowire electrode on glass with 60−80% total optical transparency.[15] The reported light scattering by Hu et al.[15] then translates to haze, which is defined as the ratio of the difference in total and specular transmittance to that of the total transmittance, of 16−28%. Even if the overall transmittance is high, the blurriness due to haze can make the Ag nanowire electrode unsuitable for display applications that require high transparency. Therefore, research on methodologies for reducing haze down to the typical levels of ITO of 1−3% is

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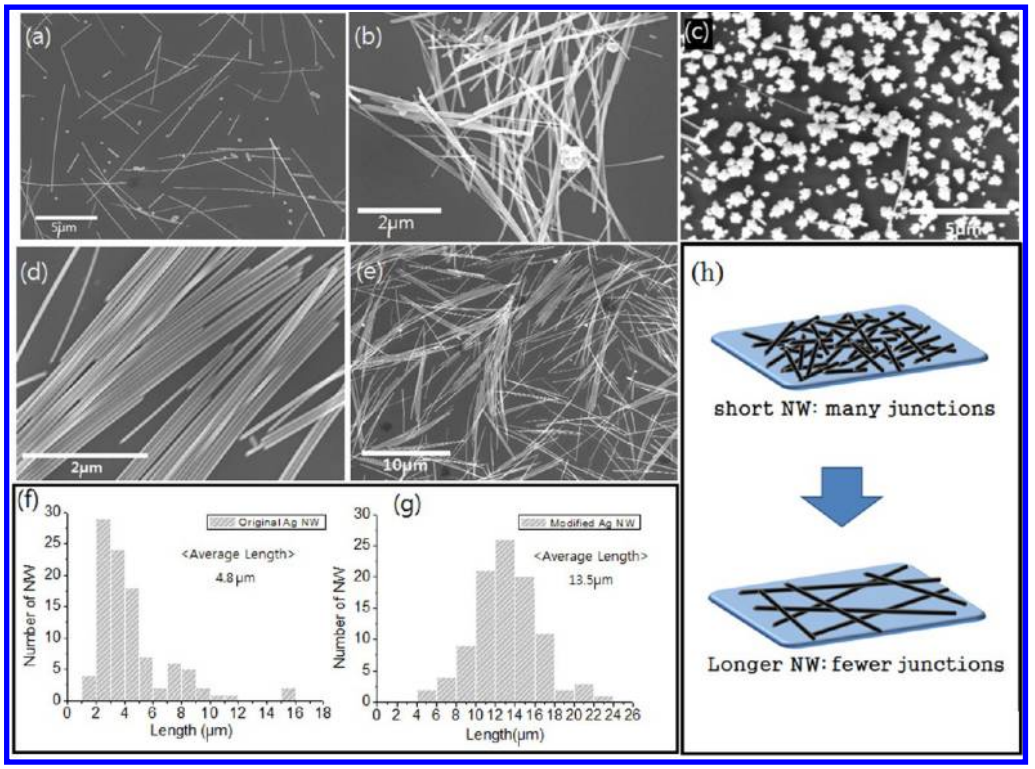

Figure 1. SEM images of the Ag nanowires synthesized using (a) the original polyol reduction method,[11] (b) with the addition of KBr, (c) with the addition of KBr as well as by replacing AgCl with NaCl (titrated), (d,e) with the addition of KBr and replacement of AgCl with NaCl (no titration). Ag nanowire distribution as determined from 6000 μm^2 for (f) original method, (g) with KBr and NaCl (no titration); (h) schematic for longer and thinner wires resulting in minumum number of junctions.

crucial for applications requiring high transparency. One approach to reducing haze is to synthesize longer and thinner nanowires that allow one to achieve the targeted sheet resistance with a smaller amount of nanowires, hence enhancing the transmittance at a given value of sheet resistance that will in turn result in a natural reduction in haze. In this work, we report a modified synthesis method for producing Ag nanowires that are longer and thinner than the nanowires synthesized using the original method by Sun et al.[14] In addition, we report a highly scalable electrostatic spray deposition methodology for uniform coating of the Ag nanowires with modified geometry onto a polycarbonate substrate.

The original polyol reduction method reported by Sun et al.[14] and used by Lee et al.[7] uses ethylene glycol (EG) as the reductant for reducing the Ag^+ ions in the solution to Ag^o to first form the Ag nanoparticle seeds. The addition of polyvinylpyrrolidone (PVP) then preferentially binds to (111) surfaces of the Ag nanoparticles that results in anisotropic growth of the nanowire along [110] directions. The resulting Ag nanowires are single crystalline and have 5-fold twin boundaries along the length of the nanowire. In the work by Lee et al.,[7] the Ag nanowires synthesized with this method were deposited onto the substrate by a drop casting method, and a post-annealing step of 200 °C for 20 min in an air furnace was used to remove the PVP that greatly reduced the sheet resistance of the nanowire network. It should be noted that the reported annealing step at 200 °C is crucial in reducing sheet resistance down to the acceptable range, and the performance of the Ag nanowire electrode degrades if a lower annealing temperature is utilized due to insufficient removal of PVP. For application of this technology to flexible devices, however, 200 °C may not be feasible with some of the commonly used substrates such as polyethylene terephthalate (PET) and polycarbonate (PC) that have glass transition temperatures in the range of 75−147 °C.[18,19] The nanowire transparent electrode made from the Ag nanowires synthesized using the original polyol reduction method by Sun et al.,[14] therefore, needs to be improved so that the targeted electrical and optical properties can be reached at a lower annealing temperature.

Because of the presence of PVP, the overall sheet resistance of the Ag nanowire electrode is mostly arising from wire-to-wire junctions, and one method for decreasing the sheet resistance of the Ag nanowire network would be to minimize the number of junctions. It has been reported in a previous study by Hu et al.[15] that junction resistance can be as high as 1×10^9 Ω although the Ag metal itself has one of the best conductivities among all metals of 1.59×10^{-8} Ω·m.[6] The high junction resistance contributes to the reported sheet resistance in the range of tens to thousands of Ω/sq as reported by Hu et al.[15] Therefore, if one can reduce the number of junctions used to form the nanowire network, the overall sheet resistance can be greatly reduced to enhance the performance of the electrode such that the nanowires may then be annealed at a lower temperature to still be able to meet the targeted sheet resistance requirement in the range of a 10−100 Ω/sq. As illustrated in Figure 1h, an improved sheet resistance per targeted transmittance can be reached by using longer and thinner nanowires since fewer junctions will be necessary to achieve the targeted transmittance, which may also be interpreted as improved transmittance per targeted sheet resistance. Another benefit of using longer and thinner nanowires is that by improving the transmittance per targeted sheet resistance, the haze will also

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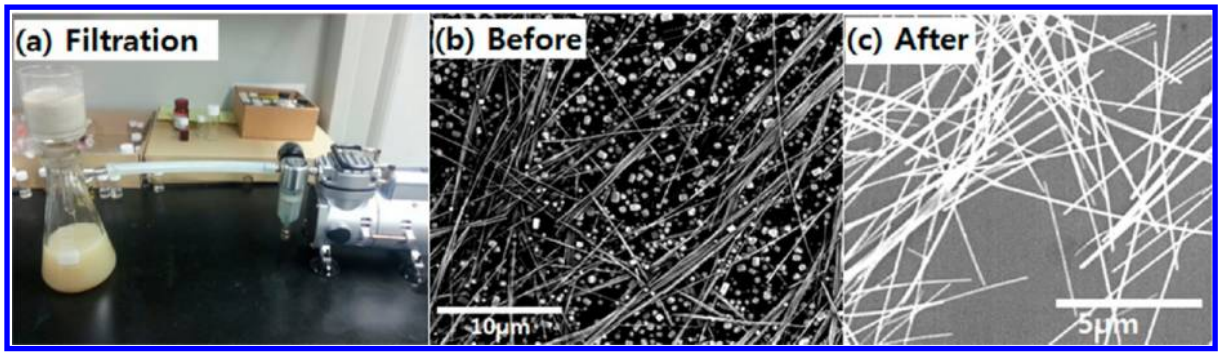

Figure 2. (a) Glass filtration setup to remove the unwanted nanoparticles from the synthesize solution, SEM image of the Ag nanowire (b) before and (c) after filtration that confirm that the glass filtration process can effectively remove unwanted nanoparticles from the solution.

naturally decrease since smaller volume of nanowires is used to form the network and thereby reducing light scattering from the nanowires.

EXPERIMENTAL SECTION

Chemicals and Materials. Polyvinylpyrrolidone (PVP, $M_w \approx$ 55000, powder) was purchased from Sigma Aldrich. Silver nitrate ($AgNO_3$, 99.0%), sodium chloride (NaCl, 99.5%), potassium bromide (KBr, 99.0%), methyl alcohol (CH_3OH, 99.5%), ethylene glycol (EG, 99.0%), and polycarbonate substrate (PC, average transmittance of 90%) were purchased from common commercial suppliers. All chemicals were used without further purification.

Synthesis of Silver Nanowire Solution. Silver nanowires were made by a solution processing method known as the polyol process[14] with some modifications. First, 6.68 g of PVP was added to 200 mL of ethylene glycol in a three necked round-bottom flask and stirred at 400 rpm using a magnetic stirrer. The mixture was then heated to 170 °C, and 0.1 g of KBr, 0.2 g of NaCl, and 2.793 g of $AgNO_3$ were added to the solution and stirred at 200 rpm. The solution was then kept at 170 °C for 4 h to allow the Ag nanowire growth reaction to take place and then was cooled down to room temperature. The nanowire solution was filtered using a glass filter in order to get rid of particles that can reduce transmittance. Collected silver nanowires were finally dispersed in methanol according to the desired concentration.

Fabrication of Silver Nanowire Electrode. The silver nanowire solution with an optimized concentration of 2.5 mg/mL was electrostatically sprayed on a PC substrate using a commercially available system from NanoNC, Inc. The syringe was loaded with the Ag nanowire solution and held at 30 kV while the PC substrate was held at ground at a distance of 3.5 cm away from the tip. The injection rate for the solution was 15 mL/h, and the density of the Ag nanowire deposition was controlled by the volume of the solution deposited. The process of optimizing various deposition parameters is described in more detail in the discussion section. After deposition of the silver nanowire electrode, a box furnace annealing at 120 °C for 8 h was performed to remove the PVP layer in order to reduce the junction resistance.

Nanowire Electrode Characterization. Transmittance measurements were carried out for Ag the nanowire electrode deposited on PC substrates using electro-spraying methods by using a UV−vis spectrometer (Shimadzu, UV 3600) in the range of 350−800 nm, which covers the visible light spectrum. Haze was determined by the ratio of the difference in the total (T_{tot}) and the specular (T_{spec}) transmittance measurements to the total transmittance (T_{tot}), haze = $(T_{tot} - T_{spec})/T_{tot}$, by taking the substrate as the reference. Sheet resistance measurements were measured using a four point probe (FPP-2400, maker is Dasol Eng Co., Ltd.). The morphologies of the Ag nanowires were determined using a field-emission scanning electron microscope (FEI, Sirion).

RESULTS AND DISCUSSION

In this study, we report the synthesis of longer and thinner Ag nanowires by making two key modifications to the original polyol reduction method by Sun et al.[14] The first modification was the addition of KBr to the solution before adding $AgNO_3$ that results in competition for the Ag^+ ions to lower the concentration of Ag^+ ions being reduced to form Ag nanowire. Several previous studies have shown that this procedure can create longer and thinner nanowires with an average length and diameter.[15,20] The SEM images of the Ag nanowires from the original polyol method in Figure 1a and those with the addition of KBr in Figure 1b clearly indicate lengthening of the nanowires. The second key modification used in this study was to replace the AgCl with NaCl seed such that there will be no source of Ag present in solution before we introduce the $AgNO_3$ for more controlled growth of the nanowires. For the first attempt at the modified method of utilizing the NaCl seed, the $AgNO_3$ solution was titrated which resulted in an initially high concentration of NaCl compared to the Ag^+ ions from $AgNO_3$ that caused formation of nanoparticles instead of nanowires, as shown in Figure 1c. However, when $AgNO_3$ was all added in a one-step process, it was possible to synthesize longer and thinner nanowires with high yield as shown in Figure 1d,e. The Ag nanowires with optimized geometry obtained by the above two modifications of using KBr and NaCl have an average length and diameter of 13.5 μm and 62.5 nm, respectively, as shown in the distribution plot shown in Figure 1f. For comparison, the length distributions of the Ag nanowires synthesized using the original polyol reduction and our modified methods are shown in Figure 1f,g that clearly indicate a significant enhancement in the average length from 4.8 to 13.5 μm.

Before coating a flexible substrate with the longer and thinner Ag nanowires, the unwanted nanoparticles that are mixed in with the nanowires should be removed from the solution since the nanoparticles can contribute to reduction in transmittance per given sheet resistance as they obstruct light while not being networked for a conduction pathway. A common method for separating nanoparticles from nanowires is to use a centrifuge, which is difficult to use for large scale production. By using glass filters with pore sizes of 5−10 μm (setup shown in Figure 2a), only long nanowires can be caught in the glass filter mesh while the particles are filtered out on the bottom. The Ag nanowires are then re-suspended in methanol with the desired density for a subsequent coating process. The usage of glass filtration allows for the synthesis of the solution in large quantities that can be used for large area depositions.

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The SEM images of the Ag nanowire solution before and after filtration are shown in Figure 2b,c. They confirm the effectiveness of this procedure in filtering out the unwanted nanoparticles to leave behind only the high quality, long, and thin Ag nanowires.

The Ag nanowires with optimized geometry for enhanced electrical and optical performance were then coated onto a PC substrate of 10 mm in thickness using an electrostatic spray system that utilizes a high voltage typically in the range of 15−30 kV at the tip while the substrate is held at ground. As the solution is pumped into the tip using a syringe pump, the solution will separate into small droplets due to the high electrical field, and the droplets are guided by the electric field to the surface of the substrate held at ground. Such an electrostatic spray system is a commonly used system for applying paint coats, and it is known to have higher efficiency with smaller loss in solution compared to an air spray. An air spray can result in as much as in 60−85% loss[21] while an electrostatic spray is known to have less than 5−30% loss[21] in solution since the droplets are guided by the electric field until they are deposited on the substrate. We have utilized a commercially available electrostatic spray system from NanoNC Technologies to coat the Ag nanowires that are suspended in methanol. Compared to the previous reports of silver nanowire electrode that utilized drop casting,[12] Mayer rod coating,[15] or air spray[16] of Ag nanowires that are suspended in methanol solvent, the electrospray deposition used in our study is a more convenient and efficient way to obtain uniform coating on large-scale substrates that could also be used on curved surfaces.

There are many parameters that need to be adjusted before a uniform coating of nanowires can be achieved. A few key parameters include the solution density, voltage applied to the spray tip, spray tip size, syringe pump rate, and distance between the tip and the substrate. We have explored these parameters systematically to find the optimized deposition condition that will produce a uniform coating of the Ag nanowires on a PC substrate, as listed in Table 1. For an electrostatic spray system, it should be noted that these parameters need to be adjusted for different types of substrates since the electric field build-up will be different for different materials of different thicknesses. Among various parameters listed in Table 1, the voltage applied at the spray tip was found to be the most critical parameter in achieving a uniform coating on the PC substrate. The nanowire solution was sprayed out with a smaller cone angle when a lower voltage setting was used, and the spray cone angle was increased by using a higher voltage setting as illustrated in Figure 3b. As the images of the deposited nanowire electrode at different voltage settings in Figure 3c,d indicate, agglomeration of the nanowires was observed for lower voltages while a uniform coating was achieved at a high voltage setting of 30 kV. A higher voltage supplied at the tip provided more widely spread out solution droplets which caused less agglomeration of the nanowires as they were being deposited onto the substrate. During the large-area coating process, the spray tip was moved along the *x*-axis while the stage was moved along the *y*-axis with the pitch and rate of motion as indicated in Table 1. The process is repeated 20 times, and ∼45 min is needed to coat a 15 × 15 cm area. The areal deposition can easily be scaled by utilizing a bigger stage and spray arm movements.

Table 1. Key Parameters for Uniform Coating of Ag Nanowires on PC Substrate Using an Electrospray Deposition System

electrostatic spray deposition parameters	
injection rate	15 mL/h
distance between needle and ground	3.5 cm
concentration of solution	2 mg/mL
solvent	methanol
applied voltage	30 kV
needle diameter	0.85 mm
total injection volume	8−12 mL

After the conditions for achieving a uniform coating were obtained, Ag nanowire electrodes with different nanowire densities were prepared by deposition of different volumes of the Ag nanowire solution with equal concentrations. For this study, we have chosen to set our solution concentration to 2.5 mg/mL, which was determined to be the ideal concentration for our electrostatic spray that is sufficiently dilute to prevent agglomeration as the nanowire solution is passed through the syringe pump to result in a uniform spray coating of the nanowires. SEM images of the Ag nanowire networks created from different solution volumes of 16, 12, 8.5, and 7.5 mL are shown in Figure 4. As apparent in Figure 4, a uniform coverage of the substrate was achieved in all cases by spraying the Ag nanowire with a fixed composition using a fixed high voltage supplied at the tip of 30 kV, and the difference in the density of network of Ag nanowire was solely controlled by the amount of volume sprayed onto the PC substrate.

The deposited Ag nanowires would normally require a post-annealing step of 200 °C to remove the PVP layer, but this temperature is unsuitable for the flexible PC substrate that has a glass transition temperature of 147 °C.[20] To investigate the optimal annealing conditions for Ag nanowires on a PC substrate, the Ag nanowires on PC substrates with an initial sheet resistance of 20 Ω/sq were annealed at different temperatures in the range of 80−200 °C for 1 h to monitor the reduction in resistance. As shown in Figure 4e, reduction in sheet resistance was more pronounced with an increase in annealing temperature from 100 to 120 °C, as expected, due to more removal of the PVP layer that results in reduction in resistance. However, an increase in resistance was measured above 130 °C, presumably due to the deforming PC substrate. Therefore, the optimized post-annealing condition was chosen as 120 °C for 8 h for effective removal of the PVP layer. A SEM image of our Ag nanowire electrode that is uniformly deposited on a PC substrate with an area of 225 cm^2 and is subsequently subjected to 120 °C annealing is shown in Figure 4f.

The optical and electrical performances of the electrostatic sprayed Ag nanowires with optimized geometry were measured using a UV−vis spectrometer and a four-point probe, respectively. The transmittance data across the visible wavelength spectrum for different nanowire densities is shown in Figure 5a. As expected, the transmittance increased when a smaller volume of Ag nanowire solution was sprayed, but it also resulted in an increased sheet resistance since a smaller amount of nanowires is used to form the network. This trend can be more clearly seen in Figure 5b, where the transmittance of the Ag nanowires at a wavelength of 550 nm is plotted against the respective sheet resistance. Figure 5b indicates that the longer and thinner nanowires deposited using the large scale electrostatic spray method on a PC substrate that was annealed at 120 °C resulted in performance similar to that of ITO. The

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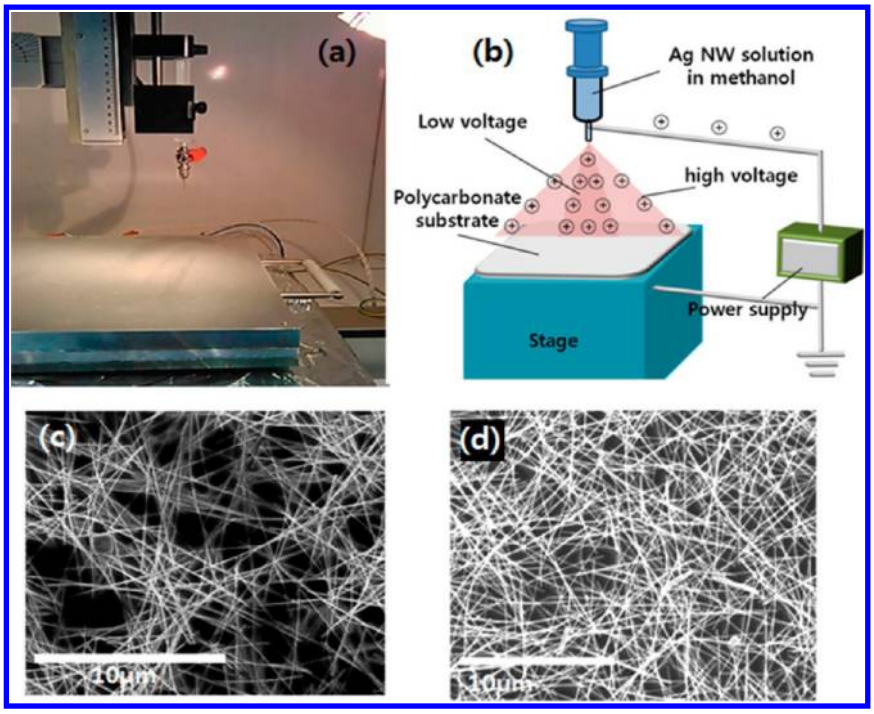

Figure 3. (a) Image of the electrostatic spray system setup; (b) schematic for the operation of the electrostatic spray system at different voltage supplied at the tip SEM image for Ag nanowire electrode with (c) a low voltage of 20 kV and (d) a high voltage of 30 kV supplied at the tip indicating that higher voltage results in more uniform deposition with less agglomeration.

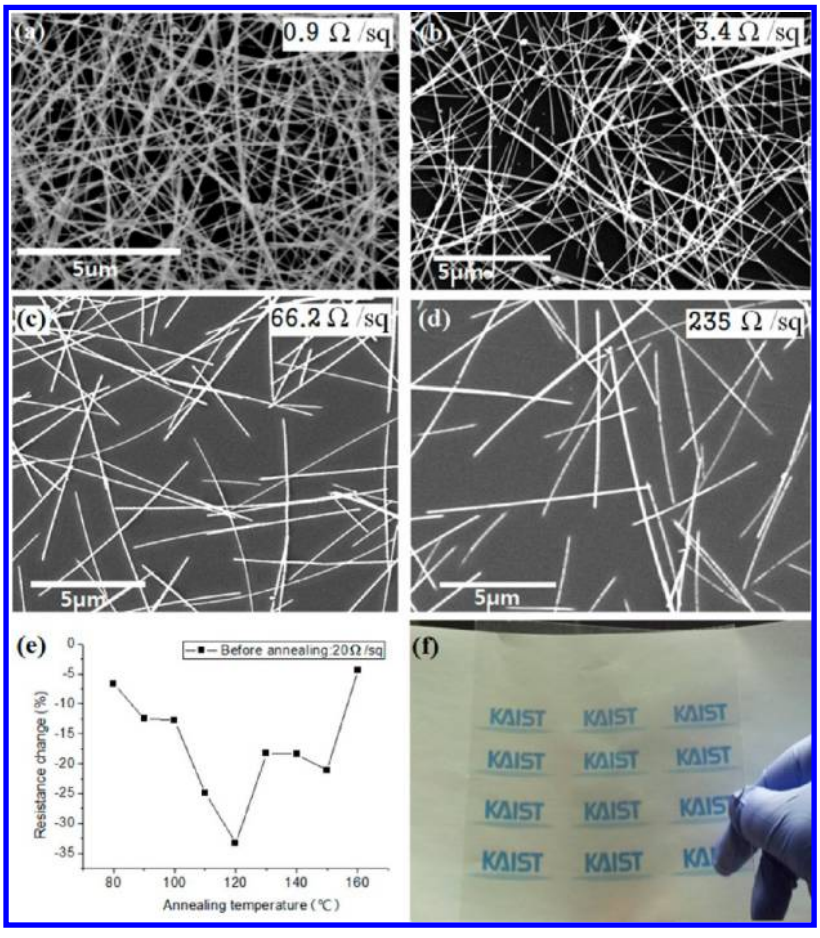

Figure 4. (a–d) SEM image of the electrostatic spray deposited nanowire network with various sheet resistance; (e) resistance change vs annealing temperature plot of Ag nanowire on PC substrate; (f) image of the large scale 15 cm × 15 cm Ag nanowire transparent electrode on PC substrate.

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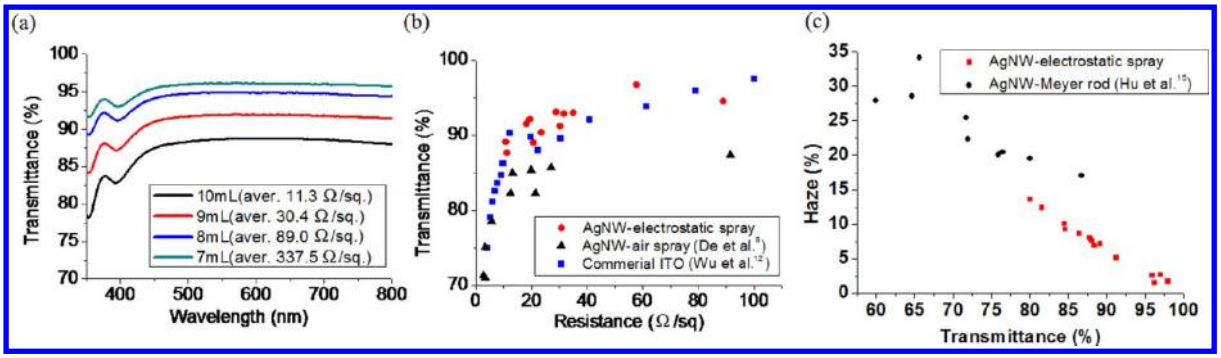

Figure 5. (a) Transmittance vs wavelength plot for Ag nanowires electrosprayed onto a PC substrate by using different solution volumes. (b) Transmittance vs sheet resistance plot of silver nanowire film with different density of Ag nanowires compared to those of commercial ITO[12] and air-sprayed Ag nanowires on PET by De et al.[8] (c) Haze vs transmittance plot for Ag nanowires electrosprayed onto a PC substrate by using different solution volumes plotted together with haze determined from the previously reported values by Hu et al. for Ag nanowires deposited onto a glass substrate using the Meyer rod method.[15]

transmittance at 550 nm for sheet resistance of 20 Ω/sq is measured to be 92.1% for our Ag nanowires, while that of ITO is 89.8%.[9]

For further comparison, the results from the study by De et al.[8] on the air-spray deposition of Ag nanowires with an average length of 6.6 μm, which is commercially available at Seashell Technologies, deposited onto a PET substrate with 100 °C of post-annealing[8] are also plotted in Figure 5b. It is clear from the comparison plot of transmittance vs sheet resistance that the electrosprayed Ag nanowires from this study are reported to have superior transmittance per given sheet resistance. At 20 Ω/sq, the transmittance at 550 nm is 81% and 87% from the work by De et al.[8] and from this study, respectively. Although both methods are efficient methods for spray coating, the methodology presented here combines modifications made to the Ag nanowires that clearly showed an enhancement in the overall performance of the Ag nanowire electrode.

It should be noted that our electrostatic sprayed Ag nanowires on PC substrate with a low annealing temperature of 120 °C is showing similar performance to that of ITO, while many of the previous studies of Ag nanowire transparent electrodes used glass as the substrate, which allowed a higher annealing temperature of 200 °C. The key to the outstanding electrical and optical performance of our Ag nanowire transparent electrode on a PC substrate that is subjected to a lower annealing temperature is ,therefore, the modified Ag nanowire synthesis for producing longer and thinner nanowires. The Ag nanowire metwork formed using the modified synthesis method allows the same sheet resistance to be reached with a smaller volume of Ag nanowires with a minimum number of junctions. The enhanced transmittance per given sheet resistance also led to a reduction in haze as shown in Figure 5c, where the haze determined from $(T_{tot} - T_{spec})/T_{tot}$ is significantly lower than the reported values from Hu et al.[15] for Ag nanowires synthesized from the original polyol reduction method coated on a glass substrate.

CONCLUSION

In summary, a modified synthesis method for creating thinner and longer nanowires was developed by the addition of KBr and by using NaCl seed instead of the AgCl seed. Electrostatic deposition of longer and thinner Ag nanowires on a PC substrate subjected to a low annealing temperature of 120 °C was demonstrated. Characterization of the Ag nanowire electrode on PC substrate indicates a comparable performance to that of ITO even though a lower annealing temperature was adopted for deposition onto a flexible PC substrate. The developed Ag nanowire network results in transmittance of 92.1% at a wavelength of 550 nm with a sheet resistance of 20 Ω/sq. The outcomes of this study, therefore, will allow for synthesis and low cost and highly scalable deposition of Ag nanowires with improved transparency per targeted sheet resistance for flexible displays, electronics, and solar cell applications.

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Notes

The authors declare no competing financial interest.

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