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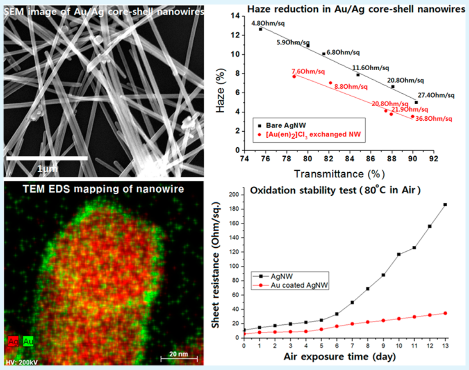
Highly Transparent Au-Coated Ag Nanowire Transparent Electrode with Reduction in Haze

Taegeon Kim,[†,‡] Ali Canlier,[†,‡,§] Changsoon Cho,[‡] Vepa Rozyyev,[‡] Jung-Yong Lee,[‡] and Seung Min Han*[,‡]

[‡]Graduate School of Energy Environment Water and Sustainability, Korea Advanced Institute of Science & Technology, Daejeon 305-701, Korea

[§]Department of Materials Science & Nanotechnology Engineering, Abdullah Gül University, 38039 Melikgazi, Kayseri, Turkey

Supporting Information



ABSTRACT: Ag nanowire transparent electrode has excellent transmittance and sheet resistance, yet its optical haze still needs to be improved in order for it to be suitable for display applications. Ag nanowires are known to have high haze because of the geometry of the nanowire and the high light scattering characteristic of the Ag. In this study, a Au-coated Ag nanowire structure was proposed to reduce the haze, where a thin layer of Au was coated on the surface of the Ag nanowires using a mild $[Au(en)_2]Cl_3$ galvanic displacement reaction. The mild galvanic exchange allowed for a thin layer of Au coating on the Ag nanowires with minimal truncation of the nanowire, where the average length and the diameter were 13.0 μm and 60 nm, respectively. The Au-coated Ag nanowires were suspended in methanol and then electrostatically sprayed on a flexible polycarbonate substrate that revealed a clear reduction in haze with a 2–4% increase in total transmittance, sheet resistance ranges of 80–90%, and 8.8–36.8 Ohm/sq. Finite difference time domain simulations were conducted for Au-coated Ag nanowires that indicated a significant reduction in the average scattering from 1 to 0.69 for Au layer thicknesses of 0–10 nm.

KEYWORDS: *transparent electrode, haze, Au-coated Ag nanowire, galvanic exchange, oxidation resistance*

INTRODUCTION

Recently, new electronic devices such as thin-film solar panels, light-emitting diodes (LED), flexible displays, and noninvasive biomedical devices, which require the usage of flexible transparent electrodes, are receiving much attention. Indium tin oxide (ITO) is the most widely used material for transparent electrode owing to its high transmittance and low sheet resistance ($T = 90\%$ at 89 Ohm/sq.)[1] and yet it cannot be applied to flexible devices because of the mechanical brittleness of ITO.[2] Furthermore, ITO generally requires high processing temperatures in the range of 300–400 °C to achieve sufficient conductance,[3] and the elevated processing temperatures may not be suitable for polymer substrates commonly used in flexible devices. Therefore, there is an urgent need to replace the brittle ITO transparent electrode with an alternative flexible material with low processing temperature for future flexible display and electronic applications.

Promising candidates for replacing ITO for flexible transparent electrode include metal nanowires,[4−7] carbon nanotubes (CNT),[8−10] graphene,[11−13] and conductive polymers.[14] Metal nanowires are especially promising compared to other carbon based or conductive polymer candidate materials owing to their high conductivity. Several studies already indicated that the Ag nanowire network can result in excellent optical and electrical properties with $R_s < 100$ Ohm/sq at $T = 90\%$ that surpasses those of ITO.[3−6,15−18] The Ag nanowires are typically synthesized in solution using the polyol reduction method that was originally developed by Sun et al.[19] and was later used by Lee et al.[1] to demonstrate the potential as a transparent electrode with excellent electrical and optical performance. The Ag nanowire films are also durable against repetitive deformations because of the mechanical flexibility of the Ag nanowire network,[20−22] making this technology viable for flexible device applications. In addition, the feasibility of using simple spray-coating methods[23−25] to deposit the nanowire electrode has opened up possibilities in significantly reducing the processing costs in comparison to that of ITO.

One of the major drawbacks of using the Ag nanowire network for display applications is that the Ag nanowires cause strong light scattering due to the geometry and the optical property of Ag. High scattering can cause blurriness if used as a transparent electrode of a display, and the current industrial standard for flexible transparent electrode requires the optical haze to be below 2–3%.[26,27] In an attempt to reduce the haze,

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modifications to the original polyol reduction synthesis method[19] were made in order to create thinner and longer nanowires with reduced junction resistance thereby resulting in enhanced electrical and optical properties.[15−18,23,28] There is, however, a limit to increasing the aspect ratio for the nanowires, because it becomes increasingly more difficult to prepare a well-dispersed nanowire solution to deposit a uniform network of nanowires using highly scalable spray depositions. In the work by Kim et al.,[23] an electrostatic spray was used to prepare the nanowire transparent electrode with transmittance of 92.1% and sheet resistance of 20 Ohm/sq that resulted in haze of 4.9%, which is beyond the industrial standard for displays.[23] In the work by Kumar et al.,[28] a 2% reduction in haze by using thinner and longer Ag nanowires was reported, but further reduction in haze just by tuning the nanowire geometry remains as a challenge.

Yet another effective method for reducing haze that can be used in conjunction with high aspect ratio nanowires is to coat the surface of the Ag nanowire with another metal that can potentially reduce the surface scattering. It is well-known that the nanostructured materials have unique optical properties due to the surface plasmon resonance (SPR), where the SPR frequency depends on the size, shape, surface modification, aggregate morphology, dielectric properties, and the refractive index of surrounding medium. For example, the SPR peak of an aqueous dispersion of 13 nm spherical Au colloids is 520 nm,[29] whereas the SPR peak of a thin film of Au is 480 nm. Au and Ag have different extinction coefficients k (for thin films, k_{Ag} = 2.92, k_{Au} = 1.90 at 500 nm)[30] and different SPR is expected for Au and Ag. Ag is especially well-known for its strong SPR that results in a strong, sharp absorption peak, whereas Au has a weak, broad absorption peak in the visible light wavelengths. Therefore, different transmittance and haze are expected for the Ag and Au metal nanowires within the visible spectrum. Although the optical properties of Au nanowire network is expected to be superior to that of Ag nanowire network, pure Au nanowires synthesized using solution-based methods will suffer from a high materials' cost and the yield is expected to be lower than that of Ag nanowires from the polyol reduction method.[31] Therefore, the use of a thin Au layer coating on the Ag nanowires prepared in solution to create a Au-coated Ag nanowire structure is explored in this study and the resulting Au-coated Ag nanowires are expected to significantly reduce haze of the nanowire transparent electrode while minimizing the materials costs.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Polyvinylpyrrolidone (PVP, $M_w \approx$ 55 000, powder) and ethylenediamine were purchased from Sigma-Aldrich. Tetrachloroauric acid ($HAuCl_4 \cdot xH_2O$, 99.9%) was purchased from Alfa Aesar. 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%), ethylene diamine, anhydrous ($NH_2CH_2CH_2NH_2$, 99.0%), and polycarbonate substrate (PC, average transmittance of 90%) were purchased from common commercial supplier. All chemicals were used without further purification.

Synthesis of Au-Coated Ag Nanowires. Ag nanowires were synthesized according to a modified polyol method described in our previous work.[23] Modified synthesis for enhanced aspect ratio involved adding KBr as well as using NaCl instead of AgCl to promote anisotropic growth of the nanowires. Density of the Ag nanowires dispersed in methanol was measured by drying and weighing a measured volume of sonicated, well-dispersed Ag nanowire solution. Au coating was carried out using two different methods. First, the galvanic displacement reaction using the $HAuCl_4$ (eq 1) was carried out using 10 mL of 0.25 mM of $HAuCl_4$ that was titrated at a rate of 0.5 drops/s into the 5 mL of Ag nanowires in deionized water with density of 0.156 mg/mL while stirring at 400 rpm throughout the reaction.

$$HAuCl_4 + 3Ag \rightarrow Au + 3AgCl + HCl \quad (1)$$

Second, a milder reaction using ethylene diamine(en) complex (eq 2) was carried out using 1 mL of Ag nanowires dispersed in methanol with a density of 1.0 mg/mL, which was diluted with 19 mL of deionized water in a glass vial. The vial was placed in an oil bath at a temperature of 95 °C and stirred at 400 rpm throughout the reaction. $[Au(en)_2]Cl_3(aq)$ (5.1 mL, 0.25 mM) was then titrated at a 0.5 drop/s rate into the Ag nanowire dispersion. Precipitation of AgCl is a byproduct of the reaction, which increases the potential and thus making the exchange reaction even more favorable. However, since AgCl is a nondesired byproduct that contributes to reduction in transmittance, 5.0 mL of 0.15 M ammonium hydroxide was added 10 min after the titration to destabilize AgCl precipitate formation.

$$[Au(en)_2]Cl_3 + 3Ag \rightarrow Au + 2en + 3AgCl \quad (2)$$

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ + Cl^- \quad (3)$$

The solution mixture was cooled to room temperature within 10 min and subsequently centrifuged at 2000 rpm for 20 min to filter out nanoparticles and short nanorods. Au-coated Ag nanowires were suspended in methanol with density of 0.5 mg/mL.

Fabrication of Electrode. The Au-coated Ag nanowires dispersed in methanol with an optimized density of 0.5 mg/mL was deposited on a polycarbonate (PC) substrate using a commercially available electrostatic spray system from NanoNC, Inc. The syringe was loaded with the nanowire solution and held at 30 kV while the PC substrate was held at ground at a distance of 3.6 cm away from the tip. The injection rate for the solution was 20 mL/h, and the density of the nanowire deposition was controlled by the volume of the sprayed solution. After deposition of the Au-coated Ag nanowire electrode, a box furnace annealing at 120 °C for 8 h was performed to reduce the junction resistance further to obtain lower the sheet resistance.

Nanowire Electrode Characterization. Transmittance of the electrostatically sprayed Au-coated Ag nanowire electrode on a PC substrate was measured using a UV−vis spectrometer (Shimadzu, UV 3600) in the visible light spectrum of 400−800 nm. Total/diffusive transmittance was measured with integrating sphere which indicated the percentage of straight and scattering light after passing through the sample. In the case of specular/linear transmittance, it indicated the percentage of straight light after passing through the sample. Haze was determined by the ratio of the difference in the total $T_{tot}(\%)$ and the specular $T_{spec}(\%)$ transmittance divided by the total transmittance $T_{tot}(\%)$ by taking the substrate as a reference.

$$\text{haze } (\%) = 100(T_{tot} - T_{spec})/(T_{tot}) \quad (4)$$

Sheet resistance was measured using a four point probe (FPP-2400, maker is Dasol Eng Co., Ltd.). The morphologies of the Au-coated Ag nanowires were imaged using a field-emission scanning electron microscope (SEM) (FEI, Sirion), and the average composition of Au-coated Ag nanowires was determined from SEM-EDS. A Cs corrected transmission electron microscope (TEM) (FEI Titan cubed G2 60−300) was used to obtain high resolution images of cross-section specimen of Au-coated Ag nanowires, which was sectioned using the Ultra-Microtome (ULTRACUT UCT, LEICA, Installed at Korea Basic Science Institute). The composition map of Au and Ag was collected using the energy-dispersive spectroscopy (EDS) in TEM.

■ RESULT AND DISCUSSION

Coating the surface of the Ag nanowire with a thin Au layer is expected to reduce haze since Au is known to scatter light less effectively than Ag due to the smaller extinction coefficient.[30] In

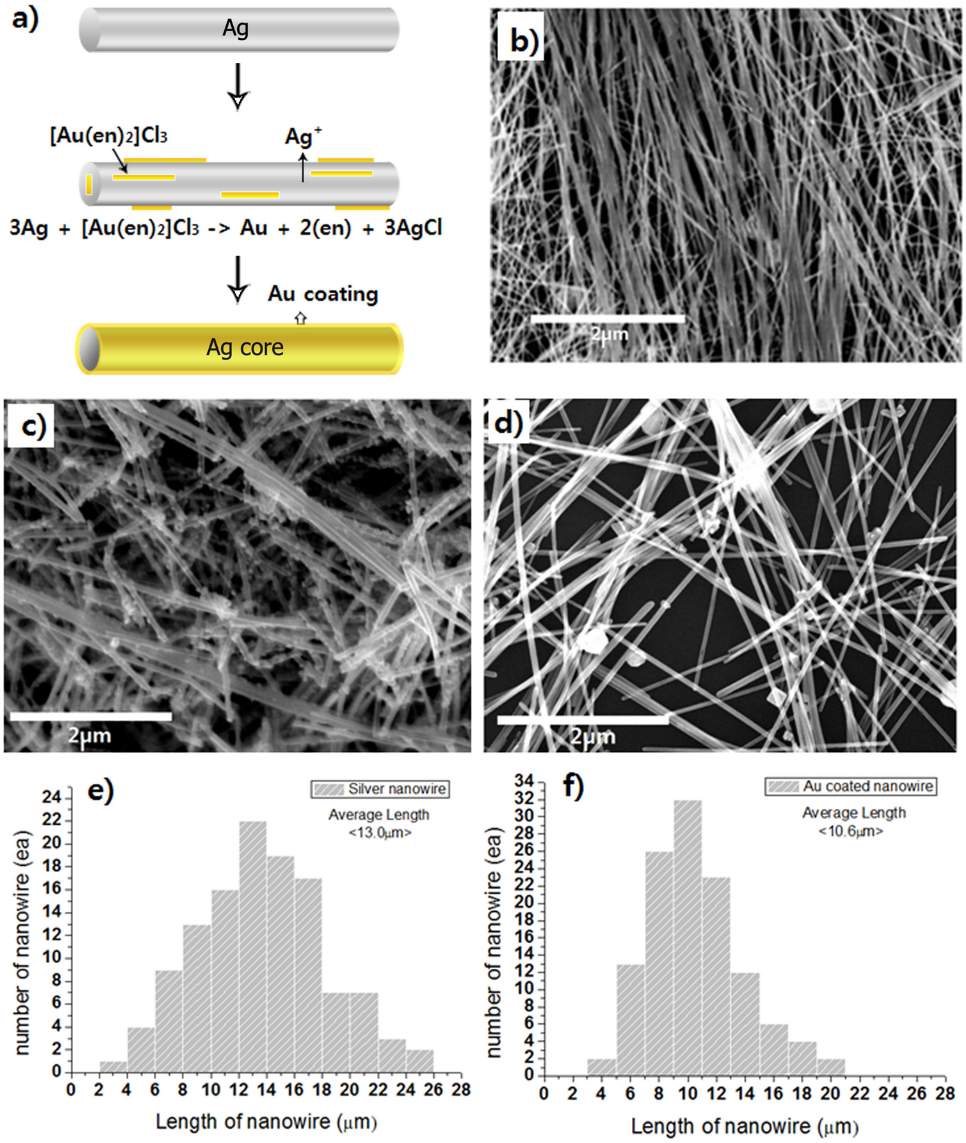

Figure 1. (a) Schematic diagram showing formation of a thin layer of Au on Ag nanowire via galvanic displacement reaction. SEM images of (b) Ag nanowires, (c) $HAuCl_4$ exchanged nanowires, (d) $[Au(en)_2]Cl_3$ exchanged nanowires. Length distribution of Ag nanowire as determined from area of 1500 μm^2 for (e) before and (f) after $[Au(en)_2]Cl_3$ galvanic exchange.

addition, another key advantage of the Au-coated Ag nanowire structure is that the Ag surface is passivated against the formation of Ag_2O or Ag_2S.[32] Ag nanowire degradation upon exposure to moist air has been studied by Khaligh et al.[33] that indicated the necessity of a protective passivation layer in order to prevent the sheet resistance from increasing beyond the desirable range when exposed to the atmosphere. Therefore, a thin Au layer coating on the top surface of the Ag nanowire with high aspect ratio, which is synthesized using the modified polyol synthesis method, has the potential to enhance the optical properties as well as the chemical stability while maintaining low material and processing cost.

The full galvanic exchange of Ag nanowire with Au was demonstrated by Sun et al.[34] where the Ag nanowire was fully exchanged with Au using $HAuCl_4$ to create Au nanoshells to show that the Ag nanowires have pentagonal shape arising from the 5-fold twin microstructure. In a galvanic exchange reaction, the difference in the reduction potential is the driving force for the exchange of atoms of the higher reduction potential with those with the lower reduction potential. For the case of galvanic exchange of Ag with Au, the reaction is given as follows

$$HAuCl_4 + 3Ag \rightarrow Au + 3AgCl + HCl \qquad (1a)$$

where one Au atomreplace three Ag atoms. Therefore, if the Ag nanowires are completely exchanged, hollow Au nanoshells will be synthesized. $HAuCl_4$-based reaction relies on a large difference in reduction potential that typically result in fast exchange rates that are suitable for synthesis of completely exchanged nanoshells, but often results in a nonuniform exchange along the length of the nanowire to cause truncation of the Ag nanowires. The use of $HAuCl_4$ was later adopted by Hu et al.[35] to demonstrate that the junction resistance can be lowered if the surface of the Ag nanowire is coated with Au using an electrodeposition of the $HAuCl_4$ solution, but the electroplating of Au was performed by immersing the already fabricated Ag nanowire network in $HAuCl_4$ solution. This methodology, therefore, involved an additional processing of immersing the whole substrate in solution, which may not be feasible with many flexible device fabrication processes. In addition, the study by Hu et al.[35] indicated that controlled galvanic exchange on the outer surface is difficult resulting in a roughened surface. Therefore, there is a need for an alternative method that will allow for a mild galvanic exchange reaction to take place to ensure that the Au layer is coated on the surface of the Ag nanowire with minimum truncation.

A well-controlled galvanic exchange method to replace just the outer layer of the Ag nanowire can be achieved by making use of an Au containing complex, where the added ligands slow down the reaction by stabilizing Au^{3+} ions[36] on the reaction interface or the surface of the Ag nanowire. Among various Au complexes, the [Au(en)$_2$]Cl$_3$ reaction system has a lower electrode potential than the HAuCl$_4$ reaction system, and the reaction is given by

$$[\mathrm{Au(en)_2}]\mathrm{Cl_3} + 3\mathrm{Ag} \rightarrow \mathrm{Au} + 2\mathrm{en} + 3\mathrm{AgCl} \qquad (2a)$$

Here, the reduction potential for [Au(en)$_2$]$^{3+}$/Au^0 is smaller than that of the AuCl^{4-}/Au^0 because (en) ligand stabilizes the Au^{3+} oxidation state against reduction.[36] In the work by Zhu et al.,[36] the difference of reduction potential between [Au(en)$_2$]$^{3+}$/Au^0 and AuCl^{4-}/Au^0 was −0.7 V (E_p[AuCl$_4^-$, 0.410 V] > E_p[Au(en)Cl$_2^+$, 0.140 V] > E_p[Au(en)$_2^{3+}$, −0.290 V]) and this reduction potential shift direction was equally occur between eqs 1 and 2. Therefore, a slower reaction occurs thereby limiting the exchange to only the outer surface of the nanowire in solution. The thickness of the Au layer can be controlled by the concentration of the Au complex in solution, and the objective of this study is to use the milder reaction to coat only the outer surface of the Ag nanowire with Au. The SEM-EDS results shown in Figure S1 in the Supporting Information showed that the overall composition from the galvanic displacement reaction is 6.4 at. %, and this composition will result in Au coating thickness of 0.91 nm for Ag nanowire with 54.68 nm in diameter (see the Supporting Information for detail).

The morphology of [Au(en)$_2$]Cl$_3$ exchanged nanowires and bare Ag nanowires are shown in the SEM images in Figure 1b, d. By using [Au(en)$_2$]Cl$_3$ exchange, the Ag nanowires are smoothly coated with a thin Au layer resulting from the mild reaction of the Au complex. In contrast, HAuCl$_4$ galvanic reaction results in non-uniform Au coating on the surface and eventually results in truncation of the Ag nanowires as shown in Figure 1c. The distribution of the length of the HAuCl$_4$ exchanged nanowires indicates an average length of less than 5 μm, which is significantly shorter than the original length of the nanowire (13 μm). Shorter nanowires will cause more junctions, which increase the sheet resistance for a given transmittance. Therefore, it is essential to use a milder reaction for Au galvanic exchange to minimize truncation of the Ag nanowires with Au layer coatings.

The morphology of the mild Au complex exchanged nanowires is shown in the SEM images in Figure 1b, d. The surface of the exchanged nanowire remained smooth, and the length distribution plot in Figure 1e, f indicates that the length is preserved with an average of 10.5 μm, which is closer to the original length of 13.0 μm. The longer Au-coated Ag nanowires in comparison to those from the HAuCl$_4$ reaction can, therefore, minimize the number of junctions between the nanowires to result in a lower sheet resistance for the same total transmittance.

Additionally, Ag$^+$ easily reacts with Cl$^-$ so that the AgCl precipitate formation occurs spontaneously during the [Au(en)$_2$]Cl$_3$ galvanic exchange. The AgCl tends to precipitate on nearby active sites of the nanowire and can deposit on the surface of the Au layer. To avoid AgCl formations, galvanic exchange solution was kept at around 95 °C in order to increase the solubility of AgCl. Any remaining AgCl precipitates were washed away with NH$_3$ solution after the galvanic exchange. The morphology of Au-coated Ag nanowires with and without NH$_3$ washing was confirmed by SEM images shown in Figure 2a, b that clearly showed removal of the AgCl precipitates around nanowires after NH$_3$ treatment.

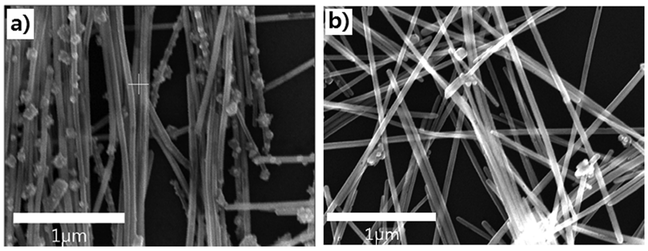

Figure 2. SEM images of Au-coated Ag nanowires (a) without and (b) with NH$_3$ wash during [Au(en)$_2$]Cl$_3$ exchange.

To confirm the existence of Au layer on the surface of the nanowire, a composition map of the cross-sectioned Au-coated Ag nanowire was collected using TEM-EDS as shown in Figure 3b, d. The EDS mapping clearly indicates that the Au is coated on the surface of the Ag nanowire. In addition, the distribution map of Au indicates that a thin Au layer is coated along the surface of the nanowire as shown in Figure 3b, d. A cross-section image taken using a Cs corrected TEM is shown in Figure 3e that revealed the five-fold twin structure of the core Ag nanowire. Therefore, TEM analysis provided evidence that the [Au(en)$_2$]Cl$_3$ galvanic exchange coated the surface of the Ag nanowire with Au.

The Au exchanged Ag nanowires in methanol solution were electrostatically sprayed on PC substrate and the optical properties were measured using the UV−vis spectrometer as shown in Figure 4a, b. Total transmittance was measured with an integrating sphere that was compared to the specular transmittance to determine haze. Within the visible light wavelength, Ag nanowire transparent electrode showed a plasmonic peak at wavelength of 375 nm, but this plasmonic peak was nearly extinct for the Au-exchanged Ag nanowire electrode. Reduced degree of scattering is apparent in the haze plot in Figure 4a inset that compared bare Ag nanowire electrode against the Au exchanged Ag nanowire electrode. The absorption spectrum in Figure 4b for different degrees of Au galvanic exchange showed that the strong, sharp absorption peak of Ag becomes broader and weaker in intensity with a small red shift with increase in the Au concentration. Au, Ag, and Au−Ag alloy nanoparticles have also been the studied for their difference in SPR frequency and absorbance.[37] In the work by Pal et al.,[37] the authors show that the composition of the Au−Ag alloy nanoparticles can result in a SPR peak shift of within the wavelength range given by the surface plasmon absorption maxima for the Ag and Au nanoparticles at 405 and 575 nm, respectively. Therefore, the variation in the Ag plasmonic resonance peak is also an indicator that the [Au(en)$_2$]Cl$_3$ exchange has successfully altered the surface properties.

The Au-coated Ag nanowires were suspended in methanol in order to use the electrostatic spray for fabrication of the Au-

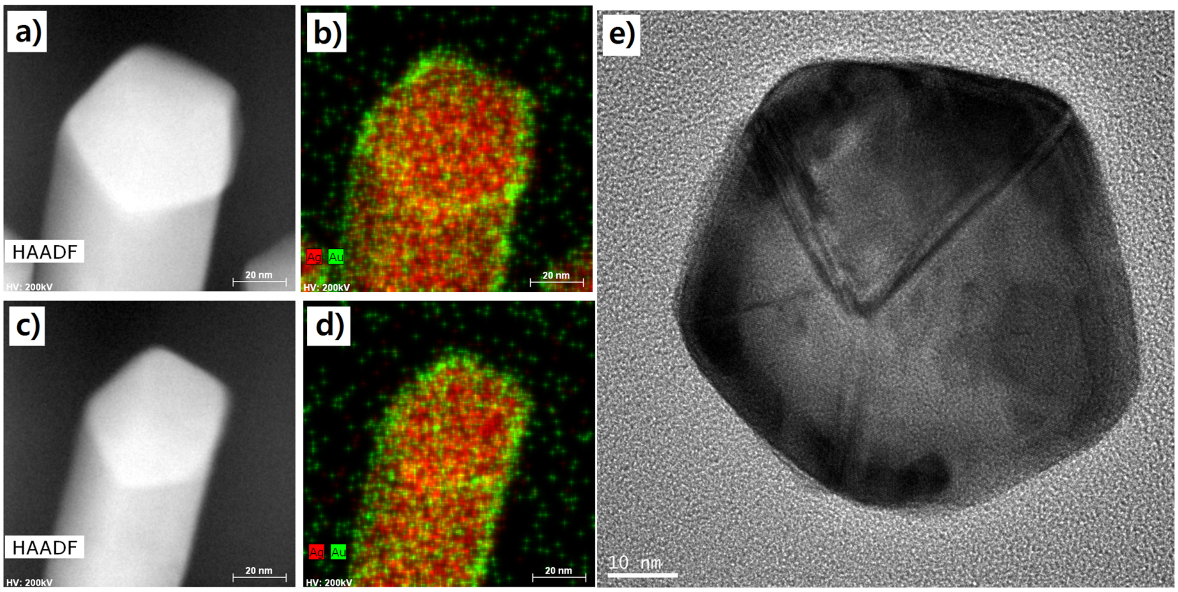

Figure 3. (a, c) Cs corrected TEM images for elemental mapping of Au and Ag, (b, d) the corresponding elemental mapping images of Ag and Au in Au-coated Ag nanowire in 200 kV, and (e) TEM image of the cross sectioned Au-coated Ag nanowire in 200 kV.

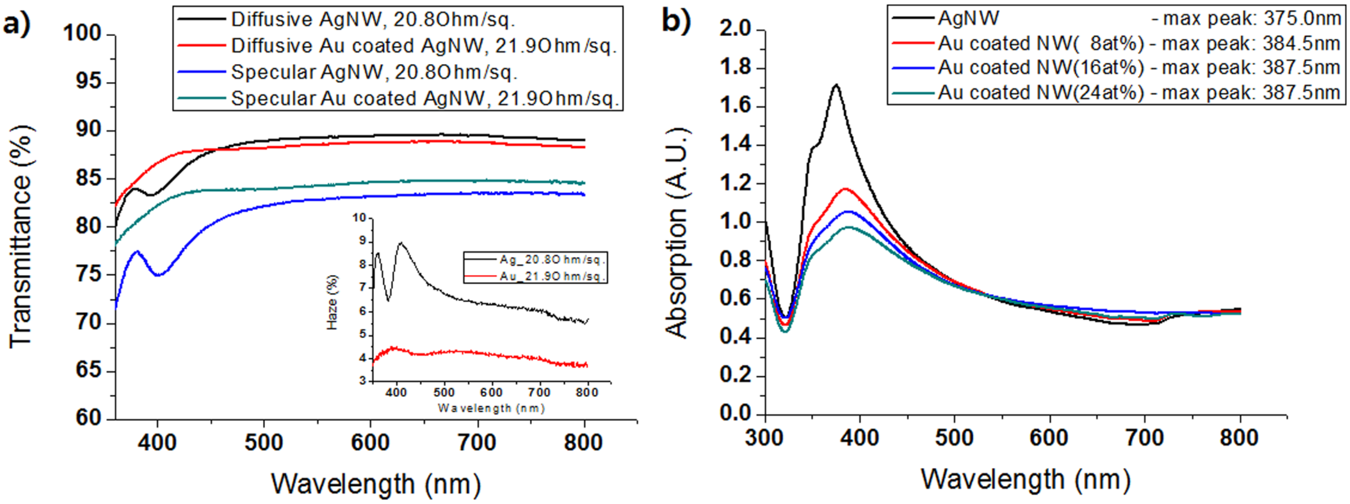

Figure 4. (a) Comparison of the UV−vis spectra of Ag nanowire films with sheet resistance of 20.8 Ohm/sq and the Au-coated Ag nanowire films with sheet resistance of 21.9 Ohm/sq. Inset: haze vs wavelength plot for Au-coated Ag nanowire films and Ag nanowire films. (b) Degradation of Ag SPR peak with increasing Au concentration from the galvanic exchange.

coated Ag nanowire electrode. The measured electrical and optical properties are shown in Figure 5, and the haze as 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}) by taking the substrate as the reference is shown in Figure 5. The electrical and optical properties of the $HAuCl_4$ exchanged Ag nanowires, which were considerably shortened in length as explained above, are shown in Figure 5. Although a clear reduction in haze of 4.5% is observed with Au coating, the sheet resistance of the electrode was as high as 1500 Ohm/sq at 87.9% transmittance, which is essentially not usable. In comparison, the $[Au(en)_2]Cl_3$ exchanged Ag nanowire electrode also showed a clear reduction in haze of 2% at 88.0% transmittance, but the sheet resistance was significantly lowered to 21.9 Ohm/sq which is similar to that of the original Ag nanowire network. Such large reduction in resistance is due to the preserved length distribution of the Au-coated Ag nanowire when the $[Au(en)_2]Cl_3$mild galvanic exchange reaction is used. Therefore, a significant reduction in haze can be achieved by coating the surface of the Ag nanowire with a thin layer of Au while maintaining similar sheet resistance and total transmittance if $[Au(en)_2]Cl_3$ is used.

To provide insights to the mechanism for reduction in haze of Au-coated Ag nanowires, the optical properties of Au-coated Ag nanowire with different Au layer thicknesses were studied using the finite-difference time-domain (FDTD) simulations. The simulations employing 2D total field scattered field (TFSF) light source were performed in an air medium with mesh size of 0.3 nm. The optical constants of Au and Ag were acquired from literature[30] and the simulation results of TE and TM modes were averaged. An idealized case of the Ag nanowire with different Au layer thicknesses that were exchanged 1:1 with constant outer diameter was used for simplicity as illustrated in the schematic shown in Figure 6a.

Light scattering for the Ag nanowires decreased with increase in the Au layer thickness while the total absorption increased as

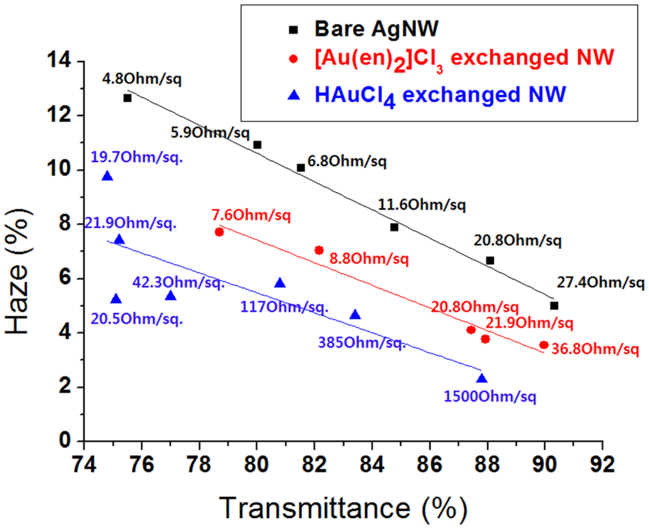

Figure 5. Comparison of haze and transmittance for the transparent films fabricated with bare Ag nanowires, the Au-coated Ag nanowires made using HAuCl$_4$ exchange, and the Au-coated Ag nanowires made using the [Au(en)$_2$]Cl$_3$ exchange and NH$_3$ treatment. Sheet resistance for each sample is also stated on the plot.

shown in Figure 6b and c. Such trend is attributed to the difference in the basic optical properties of Ag and Au.[38] Because the dielectric constant of Ag has little imaginary part in the visible range, the absorption cross-section is small and the scattering property is dominant (black lines in Figure 6b, c). On the other hand, Au has relatively higher absorption and suppressed scattering characteristics compared to those of Ag (dark yellow lines in Figure 6b, c). Figure 6b and c show that the core−shell property becomes close to that of Au as the shell thickness increases and that effect is mostly saturated near the thickness of 15 nm. Despite smaller peak reduction and larger increase of absorption in longer wavelength shown in Figure 6c compared to the experimental data in Figure 4b, the trend of absorption spectrum with the increase in the Au layer thickness was well-matched with the experimental absorption spectrum. Although the FDTD simulations indicate that the 10 nm thickness of Au layer is optimal for scatter reduction, the fact that the galvanic exchange replaces 3 Ag atoms with 1 Au atom make it difficult to uniformly coat the outer surface of Ag without formation of voids. Therefore, the optimum thickness of Au layer without truncation is much smaller than simulation.

Another advantage of the Au-coated Ag nanowire is that the nanowire can be protected against any oxidation or sulfurization to form Ag$_2$O or Ag$_2$S when exposed to the ambient atmosphere. To observe the passivation effect of the Au layer, the Ag nanowire electrode and the Au-coated Ag nanowire samples were each heated in air to 80 °C using a hot plate, and the sheet resistance of the samples were monitored every day. The resulting evolution of the sheet resistance over time is shown in Figure 7c, where the Au-coated Ag nanowire electrode showed significantly slower increase in sheet resistance compared to the pure Ag nanowire electrode. Coating Au layer on the surface of Ag nanowire is effective in protecting the Ag nanowire from oxidation and surfurization, and therefore the Au layer resulted in higher chemical stability and reliability in addition to the reduction in haze.

3. CONCLUSION

In this study, Au galvanic exchange using [Au(en)$_2$]Cl$_3$ was successfully used to coat the surface of the Ag nanowire with a thin layer of Au. The mild galvanic exchange reaction resulted in a slower reaction rate to only replace the outer surface with Au without truncating the Ag nanowires. Methanol suspensions of Au-coated Ag nanowires were electrostatically deposited on polycarbonate substrate and evaluated for the electrical, optical properties. Haze reduction for the case of Au-coated Ag nanowire with average concentration of 6.4 at. % Au was in the range of 2−4% for total transmittance of 80−90%. The presence of the Au layer resulted in reduction and red-shift of the Ag plasmonic peak, and the FDTD simulations confirmed that the exchange of Ag with Au outer surface can result in significant reduction in scattering and haze. Furthermore, Au layer was confirmed to be an effective passivation layer against oxidation and sulfurization, where the Au-coated Ag nanowire electrode showed significantly smaller increase in sheet resistance compared to the Ag only nanowire electrode when tested in air at 80 °C. Therefore, the outcomes of this study indicate that the Au-coated Ag nanowires can result in a low-haze, chemically stable, and therefore, more reliable transparent

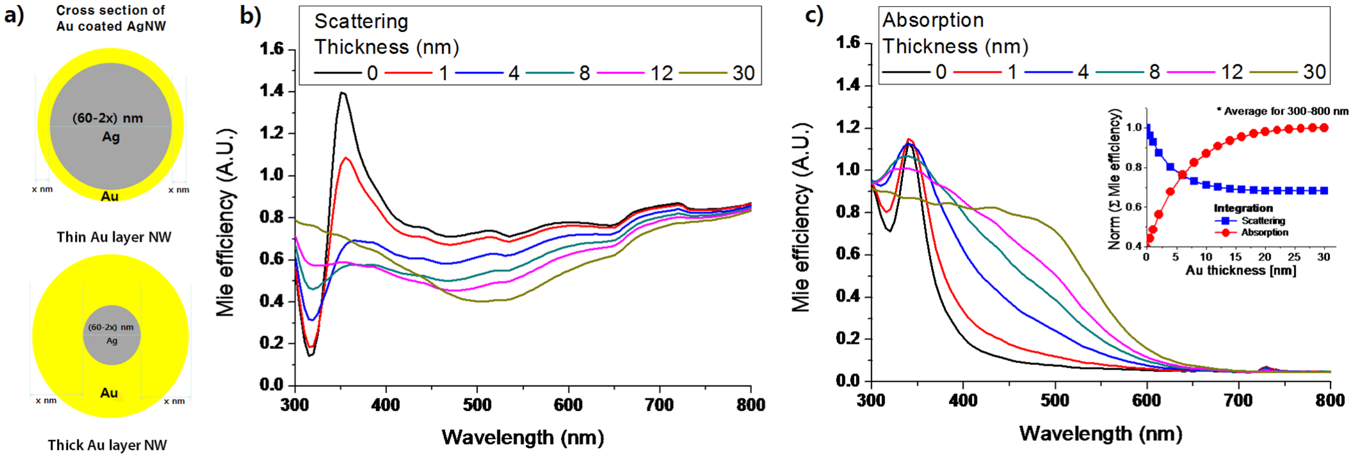

Figure 6. (a) Schematic illustration of varying thicknesses of Au modeled in 2D FDTD simulations (b) scattering and (c) absorption over the wavelength 300−800 nm according to the Au thickness obtained from the FDTD simulations in (TE + TM) mode. Inset: normalized average scattering and absorption over the wavelength 300−800 nm according to the thickness of Au layer.

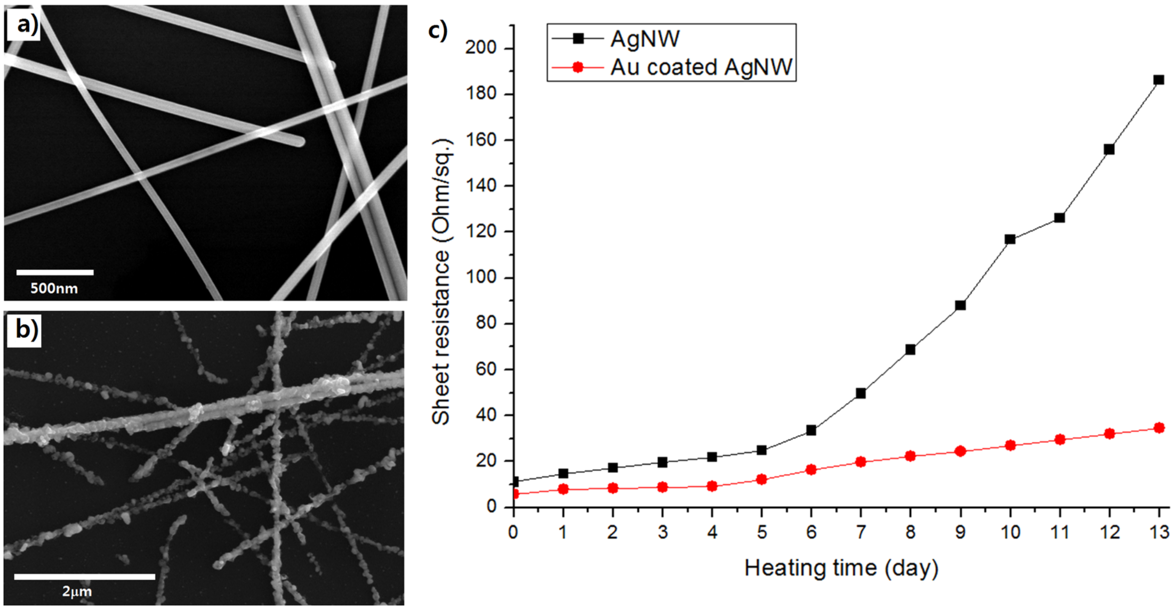

Figure 7. (a) SEM images of the Ag nanowire electrode before and (b) after 17 days heating at 80 °C in air. (c) Evolution of the sheet resistance while heating at 80 °C in air for the Ag nanowire and Au-coated Ag nanowire electrode.

electrode that can be applied to flexible displays or other electronics requiring high visibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information includes calculation of the Au layer thickness based on the average composition of Au from SEM-EDS. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: smhan01@kaist.ac.kr, .

Author Contributions

[†]Authors T.K. and A.C. contributed equally

Notes

The authors declare no competing financial interest.

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