

## THIN FILMS OF INERT METAL NANOWIRES FOR DISPLAY APPLICATIONS

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### Abstract

Ag nanowire transparent electrode has excellent transmittance (90%) and sheet resistance (20 Ohm/sq), yet there are slight drawbacks such as optical haze and chemical instability against aerial oxidation. Chemical stability of Ag nanowires needs to be improved in order for it to be suitable for electrode applications. Coating Ag nanowires with a thin layer of inert metals such as Au and Pd through galvanic exchange reactions may enhance the chemical stability of Ag nanowire films highly and also helps to obtain lower haze. In this study, coating of thin Au and Pd layers has been applied successfully onto the surface of Ag nanowires. Usually coatings are carried out by salts such as H<sub>2</sub>AuCl<sub>4</sub> and K<sub>2</sub>PdCl<sub>4</sub> in order to make nanotubes. In this study, novel ethylenediamine(en) complexes of inert metal cations with mild oxidation power were prepared in order to oxidize Ag atoms partially on the surface through galvanic displacement. The mild galvanic exchange allowed for a thin layer (1-4 nm) of inert metal coating on the Ag nanowires with minimal truncation of the nanowire, where the average lengths and the diameters were between 10~14 μm and 55~65 nm, respectively. The crystalline structure of the shell was formed epitaxially on the surface. The new Ag nanowires were suspended in methanol and then electrostatically sprayed on glass and flexible substrates. It was revealed that average total transmittance remain around 90% within visible spectrum region (400-800 nm) whereas sheet resistance rises up to 175 Ohm/sq. Very thin layer of inert metal costs low, though this may render an excellent catalyst for applications such as fuel cell and organic synthesis, whereas transparent films of inert metal-coated Ag nanowire can be utilized as working electrodes for spectro-electrochemical cells as well.

**Keywords:** transparent electrode, Au, Pd coated Ag nanowire, galvanic exchange, oxidation resistance, fuel cell

### INTRODUCTION

Transparent electrodes of metal nanowires have recently been a hot research topic for transparent electrodes as an important component of flexible displays, noninvasive biomedical devices, organic light emitting diodes (OLED) and solar panels.<sup>1,2</sup> Indium tin oxide (ITO) is the most popular material used for transparent electrode component of related devices.<sup>3,4</sup> However, on account of some drawbacks of ITO films such as brittleness, scarcity of Indium resources, and high material and manufacturing costs, carbon nanotubes,<sup>5-7</sup> graphene,<sup>8-10</sup> and metal nanowires<sup>11-14</sup> have been proposed as alternative transparent electrodes to replace ITO. In particular, requirement of high processing temperature in the range of 300–400 °C for ITO is a huge drawback for flexible display applications, which employ plastic substrates in general.

Recent studies already indicated that the Ag nanowire network can surpass ITO with excellent optical and electrical properties with  $R_s < 100$  Ohm/sq at  $T = 90\%$ .<sup>15-16</sup> The Ag nanowires are typically synthesized in solution using the polyol reduction as previously done in our work.<sup>14</sup> The Ag nanowire films can preserve optical and electrical strength even after numerous bending, which makes it suitable for flexible devices.<sup>17-18</sup>

Also simplicity of large-scale spray-coating of Ag nanowires onto substrates of various materials and geometries made it possible to reduce ITO costs greatly.

One of the major drawbacks of Ag nanowire films in display applications is the highly scattering of light through Ag silver surface, which is otherwise expressed as high haze. This phenomenon is commonly explained with the strong Surface Plasmon Resonance (SPR) effect of Ag. In order to reduce this effect in display applications, we proposed coating thin layers of Au and Pd around Ag nanowires via a galvanic displacement reaction.<sup>19</sup> This coating slightly altered the optical characteristics of Ag nanowires that resulted in reduced haze (from 8-15% to 2-4%). In addition, Au and Pd shell surrounding the Ag core enhanced the chemical stability of nanowire films highly. For example, heating at 80 °C in air for 2 weeks caused only a slight increase in the sheet resistance of the Ag@Au nanowire film whereas the sheet resistance of Ag nanowire film increased more than ten folds with the same treatment.

In order to manipulate optical nature of Ag nanowires and apply the films for a wider area of applications, we coated Ag nanowires with thin layers of Au and Pd in solution. As the refractive indices and extinction coefficients of Ag and other metals are different, it can be expected to see different haze for Ag nanowire films and newly-coated nanowires. In addition, Au and Pd are more resistant against oxidation because of higher standard reduction potential of its cation compared to that of silver cation. Thus, a higher chemical stability can be expected for Ag@Au and Ag@Pd core/shell nanowire films. Nevertheless, Ag@Pd nanowire film is supposed to be inferior to Ag nanowire film in terms of electrical conductivity. Bulk resistivity of Ag is 15.87 nΩ·m and that of Au is 22.14 nΩ·m, whereas that of Pd is 105.4 nΩ·m. This is expected to increase the sheet resistance of the films compared to that of Ag nanowire films.

Inert metal coated nanowires and films of those can render excellent catalysts since surface area plays an important role in catalysis applications. Very thin layer (shell) requires little amount of inert metal and easiness of the galvanic exchange process and spray-coating may open up new possibilities of catalysis applications. Pd compounds in various forms and also Pd nanoparticles are widely used as catalyst in numerous reactions and syntheses.<sup>20-22</sup> Pt and Au nanoparticles-embedded catalysts also find wide application area. Nanoparticles increase the rate and yield of the reactions extensively where surface area is the key function which determines the rate.<sup>21</sup> Fuel cell catalysts with Pd content produce higher energy than without Pd as in Pt catalyst or Pt/Ru catalyst.<sup>23</sup> For example, formic acid fuel cells work well with Pd catalysts,<sup>24</sup> which also contributes to recycling CO<sub>2</sub> and controlling its emission. According to these results, we can propose new Au and Pd catalyst systems based on Ag@inert-metal core/shell nanowire films.

## 1. EXPERIMENTAL SECTION

**Chemicals and Materials.** Polyvinylpyrrolidone (PVP,  $M_w \approx 40\,000$ , powder), silver nitrate (AgNO<sub>3</sub>, 99.0%), tetrachloroauric acid (HAuCl<sub>4</sub>·xH<sub>2</sub>O, 99.9%), and palladium(II) nitrate dihydrate (Pd(NO<sub>3</sub>)<sub>2</sub>, ~40% Pd basis) were purchased from Sigma-Aldrich. Sodium chloride (NaCl, 99.5%), potassium bromide (KBr, 99.0%), methyl alcohol (CH<sub>3</sub>OH, 99.5%), ethylene glycol (EG, 99.0%), ethylene diamine, anhydrous (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, 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 before in our previous work.<sup>14</sup> This batch was used for all reactions. 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<sub>4</sub> (eq 1) was carried out using 6.4 mL of 0.25 mM of HAuCl<sub>4</sub> that was titrated at a rate of 0.5 drops/s into the 5 mL of Ag nanowires in deionized water with density of 0.1 mg/mL while stirring at 400 rpm throughout the reaction.



Second, a milder reaction using ethylenediamine(en) complex (eq 2) was carried out using 1 mL of Ag nanowires dispersed in methanol with a density of 1.2 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.  $[\text{Au}(\text{en})_2]\text{Cl}_3(\text{aq})$  (6.1 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 undesired 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.



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.

**Synthesis of Pd-Coated Ag Nanowires.** Previously synthesized Ag nanowires were used. Pd coating was carried out using three different methods. First, the galvanic displacement reaction using the  $\text{Pd}(\text{NO}_3)_2$  (eq 4) was carried out using 21.4 mL of 0.25 mM of  $\text{Pd}(\text{NO}_3)_2$  that was titrated at a rate of 0.5 drops/s into the 50 mL of Ag nanowires in deionized water with density of 0.116 mg/mL while stirring at 400 rpm throughout the reaction. pH of Pd(II) solution was made 4.0 by addition of dilute nitric acid prior to titration.



Second, a milder oxidizing complex reagent of  $[\text{Pd}(\text{en})_2](\text{NO}_3)_2(\text{aq})$  (eq. 5) was prepared in situ by mixing 1 eq.  $\text{Pd}(\text{NO}_3)_2(\text{aq})$  with 4 eq. ethylenediamine(en)<sub>(aq)</sub>(excess). pH was made 5.0 by addition of dilute nitric acid prior to titration. Titration was carried out using 1 mL of Ag nanowires dispersed in methanol with a density of 1.16 mg/mL, which was diluted with 19 mL of deionized water in a glass vial. The mixture was stirred at 400 rpm throughout the reaction.  $[\text{Pd}(\text{en})_2](\text{NO}_3)_2(\text{aq})$  (4.3 mL, 0.25 mM) was then titrated at a 0.5 drop/s rate into the Ag nanowire dispersion.



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

**Fabrication of Electrode.** Electrostatic spray coating of the inert metal coated Ag nanowires was carried out as in our previous works.<sup>14,19</sup> Ag@Au and Ag@Pd core/shell nanowires were dispersed in methanol with an optimized density of 0.5 mg/mL. It 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 or Pd-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 or Pd-coated Ag nanowire electrode on a PC substrate was measured using an UV-vis spectrophotometer (Shimadzu, UV-1800&Perkin-Elmer, LAMBDA 950) in the visible light spectrum of 300–800 nm.

Sheet resistance was measured using a four point probe (Lucas Lab 302) connected to a PC which runs a Gamry software via a potentiostat (Gamry, Interface 1000). The morphologies of the Au or Pd-coated Ag nanowires were imaged using a scanning electron microscope (SEM) (Stereoscan S440, Leo), and the average composition of Au or Pd-coated Ag nanowires was determined from SEM-EDS. A Cs corrected

transmission electron microscope (TEM) (FEI, Tecnai G2 F30) was used to obtain high resolution images of Au-coated Ag nanowires.

An extra work of quantitative analysis was carried out for determination of Ag@Pd core/shell nanowire composition since lowest EDS energies of Ag (2.984 eV) and Pd (2.838 eV) are so close that signals almost overlap. 0.153 g of Ag@Pd core/shell nanowire was weighed after filtering, washing, drying and annealing of a product of galvanic exchange reaction. Nanowires were put in a 40 mL of concentrated HCl<sub>(aq)</sub> solution. While started to boil, 15 mL of nitric acid was added dropwise. The mixture was kept boiling until the fume evolution comes to an end. Then the solution was neutralized by addition of NaOH<sub>(aq)</sub>. A pre-weighed copper strip was dipped into the slowly stirred solution for 10 min. After the strip, it was weighed and the compositions were calculated.

## 2. RESULTS AND DISCUSSION

A thin layer of Au or Pd on Ag nanowire surface is expected to scatter light less than Ag nanowire itself due to smaller average extinction coefficients and refractive indices along visible region.<sup>25</sup> In addition, another key advantage of the inert metal coated Ag nanowire structure is that the Ag surface is passivated against the formation of Ag<sub>2</sub>O or Ag<sub>2</sub>S.<sup>26</sup> Therefore, a thin Au or Pd layer coating on the top surface of the Ag nanowire, has the potential to enhance the optical properties as well as the chemical stability while maintaining low material and processing cost.

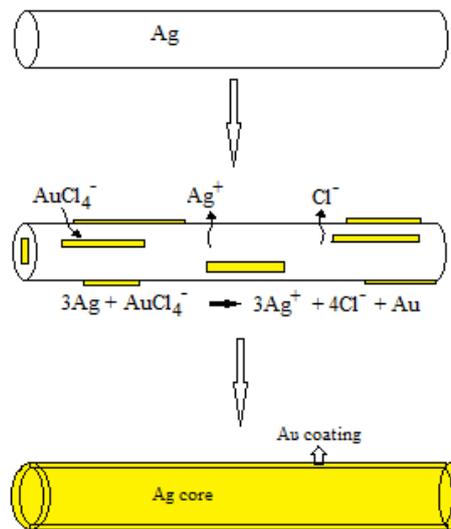
The full galvanic exchange of Ag nanowire with Au, Pt and Pd was demonstrated before in order to make nanoshells.<sup>27,28</sup> As the reduction potential of Au(III) and Pd(II) species are higher than that of Ag(I), reaction proceeds to the side where Ag dissolves and Au or Pd precipitates on the surface. Three Ag atoms are replaced by one Au atom, and two Ag atoms are replaced by one Pd atom. If a chloride compound of inert metal is used, AgCl precipitate forms if the concentrations product reaches the critical value (eq. 1). Choosing a nonchloride compound can prevent the precipitation of AgCl. However, it is difficult to find a soluble nonchloride Au(III) or Au(I) compound. Therefore, the mixture was added ammonia solution in order to remove any AgCl precipitation after Au coating titration (eq. 3). For Pd coating, a water soluble Pd(NO<sub>3</sub>)<sub>2</sub> species can be used well. Galvanic exchange reactions proceed at high rates if a large potential difference drives the reaction. High rate of electrochemical reactions may cause truncation of nanowires and unwanted particle formation may increase. In addition, layer thickness may not be homogeneous and surface might be rough.

A well-controlled galvanic exchange method to replace just the outer layer of the Ag nanowire can be achieved by making use of an inert metal containing complexes, where the chelating agents stabilize the complex compound with higher formation constants. Extra stabilization of the complexes lowers the reduction potentials to a great extent.

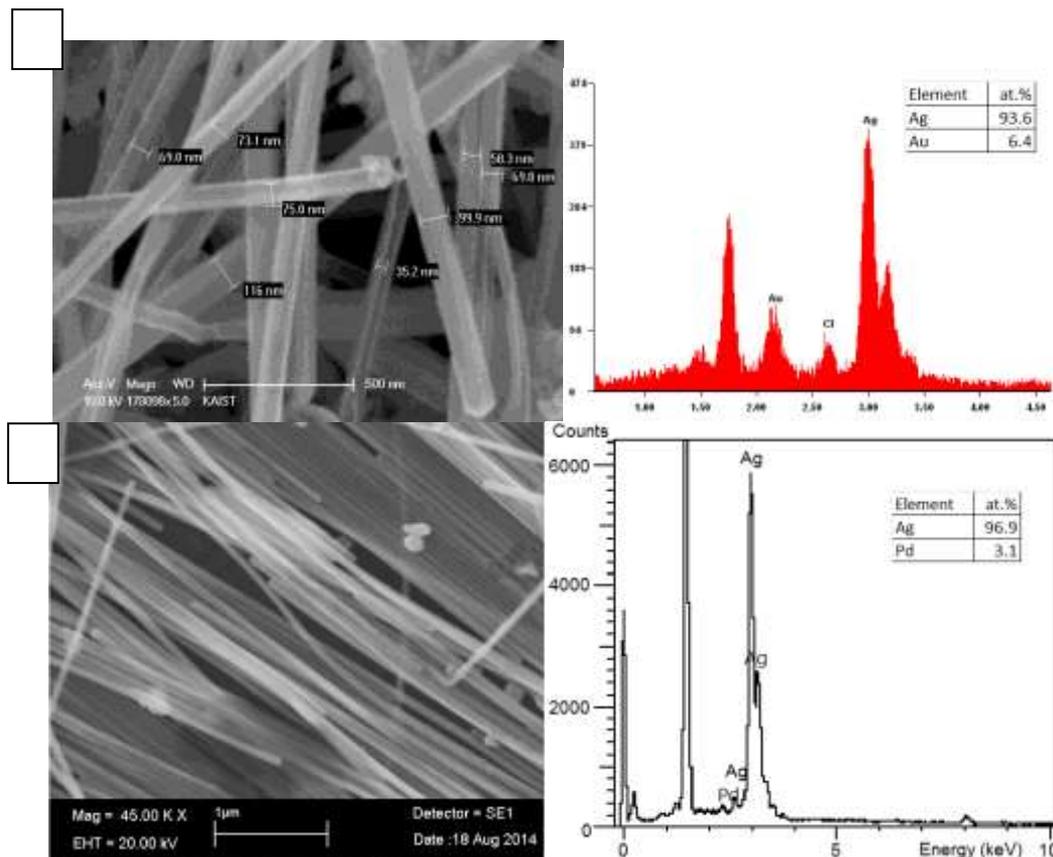


Here, the reduction potential for [Au(en)<sub>2</sub>]<sup>3+</sup>/Au<sup>0</sup> is smaller than that of the AuCl<sub>4</sub><sup>-</sup>/Au<sup>0</sup> because (en) ligand stabilizes the Au<sup>3+</sup> oxidation state against reduction.<sup>29-32</sup> In the work by Zhu et al.,<sup>29</sup> the difference of reduction potential between [Au(en)<sub>2</sub>]<sup>3+</sup>/Au<sup>0</sup> and AuCl<sub>4</sub><sup>-</sup>/Au<sup>0</sup> was -0.7 V (Ep[AuCl<sub>4</sub><sup>-</sup>, 0.410 V] > Ep[Au(en)Cl<sub>2</sub><sup>+</sup>, 0.140 V] > Ep[Au(en)<sub>2</sub><sup>3+</sup>, -0.290 V]) and this reduction potential shift direction was equally occur between eqs 1 and 2. There is no reference for comparing reduction potentials of Pd(II) species, but it is known that [Pd(en)<sub>2</sub>]<sup>2+</sup> complexes were synthesized and isolated as single-crystals.<sup>33</sup> It is same for Pd(II) complexes that reduction potential is lower than that of sole Pd(II) ion. However, pH should be kept as lower as possible in order to stop Pd(II) from forming insoluble hydroxide species.<sup>34</sup> Therefore, pH of solutions was adjusted to be within 4.0-5.0 prior to addition of chelating agent (ethylenediamine). HAuCl<sub>4</sub> has already some acidic character before ligand addition. The thickness of the inert metal layer can be controlled by the concentration

of the 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 inert metal (Figure 1).

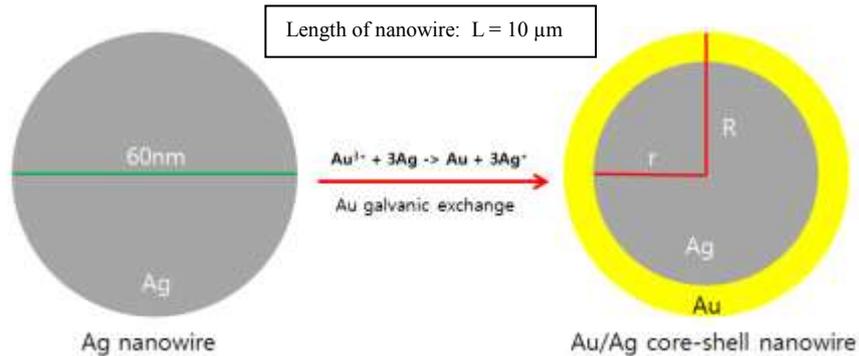


**Figure 1.** Schematical representation of Au-coating on the Ag nanowire through a galvanic displacement reaction.



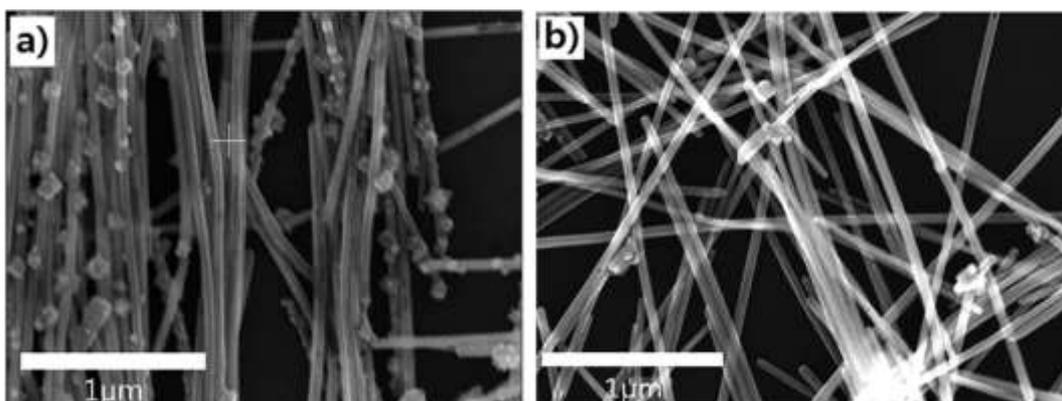
**Figure 2.** a) SEM image of Au/Ag core-shell nanowires (left) and SEM-EDS data for Au and Ag (right). b) SEM image of Pd/Ag core-shell nanowires (left) and SEM-EDS data for Pd and Ag (right).

The SEM-EDS results shown in Figure 2 showed that nanowire lengths were preserved due to little truncation with mild oxidation. Nanowire surfaces look smooth in the images. This is an evidence to homogeneous coating of nanowires. The overall composition from the galvanic displacement reaction is 6.4 at.% for Ag@Au nanowire, and it is 3.1 at.% for Ag@Pd nanowire. This composition will result in Au coating thickness of 0.91 nm for Ag nanowire with 55 nm in diameter and it is 0.40 nm for Pd coating. Layer thickness was roughly calculated by a formulation derived for cylindrical core/shell system (Figure 3). Number of atoms ( $N_{\text{atom}}$ ) were taken from EDS result,  $R_{\text{Ag}}=144.5 \text{ pm}$ ,  $R_{\text{Au}}=144.2 \text{ pm}$ ,  $R_{\text{Pd}}=137.0 \text{ pm}$ .



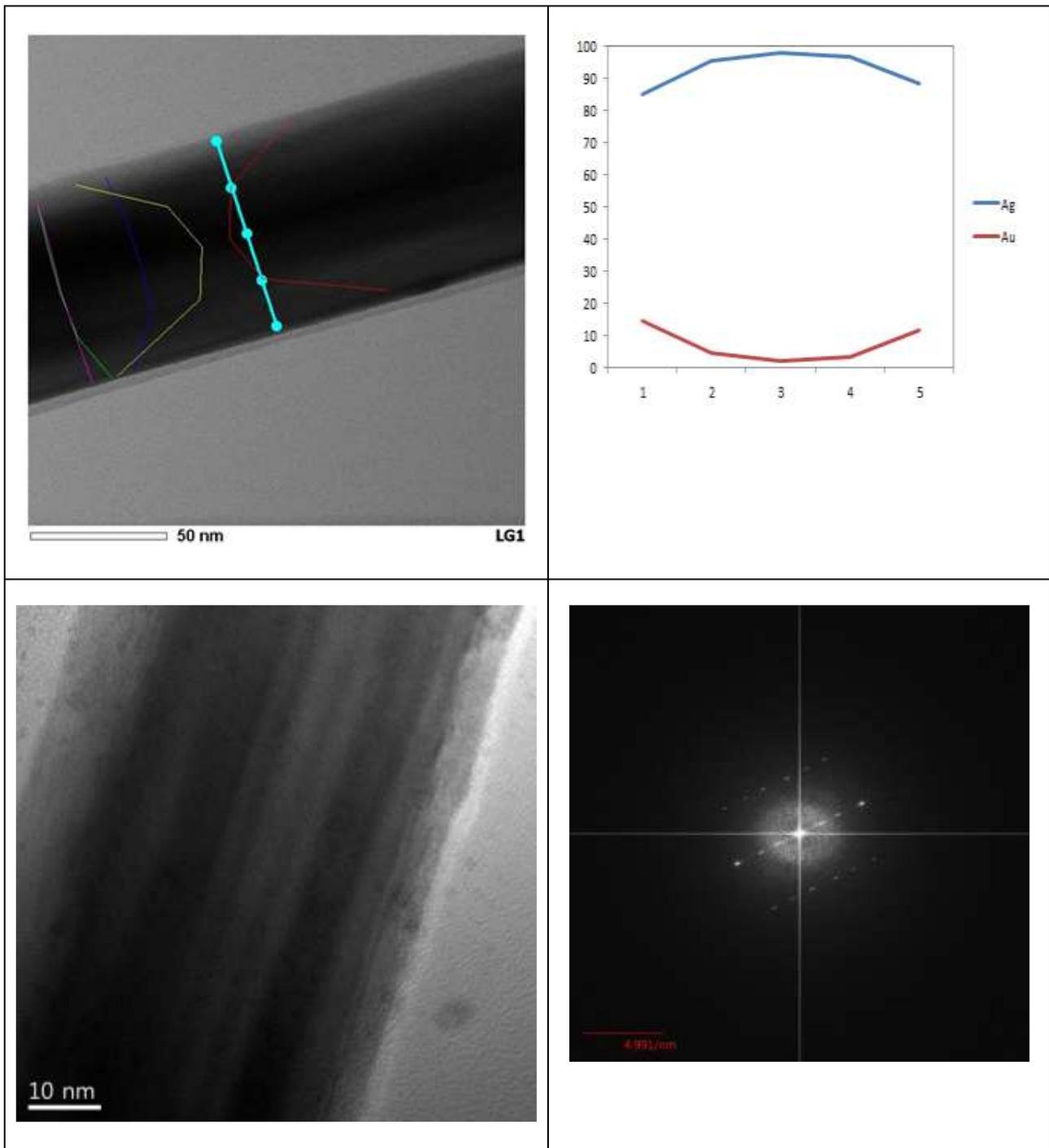
**Figure 3.** Schematic for the cross section of Ag nanowire before and after Au galvanic exchange.

The morphology of the mild Au complex exchanged nanowires is shown in the SEM images in Figure 4b. The surface of the exchanged nanowire remained smooth, and the length distribution plot indicates that the length is preserved with an average of 10.5  $\mu\text{m}$ , which is closer to the original length of 13.0  $\mu\text{m}$ . The longer Au-coated Ag nanowires in comparison to those from the  $\text{HAuCl}_4$  reaction can, therefore, minimize the number of junctions between the nanowires to result in a lower sheet resistance for the same total transmittance. Presence of ethylenediamine and further addition of ammonia help dissolution of any  $\text{AgCl}$  precipitation. Ethylenediamine itself can make complex with  $\text{Ag(I)}$ . The result of these treatments can be seen in Figure 4 for comparison.



**Figure 3.** SEM images of Au-coated Ag nanowires (a) without and (b) with  $\text{NH}_3$  wash during  $[\text{Au}(\text{en})_2]\text{Cl}_3$  exchange.

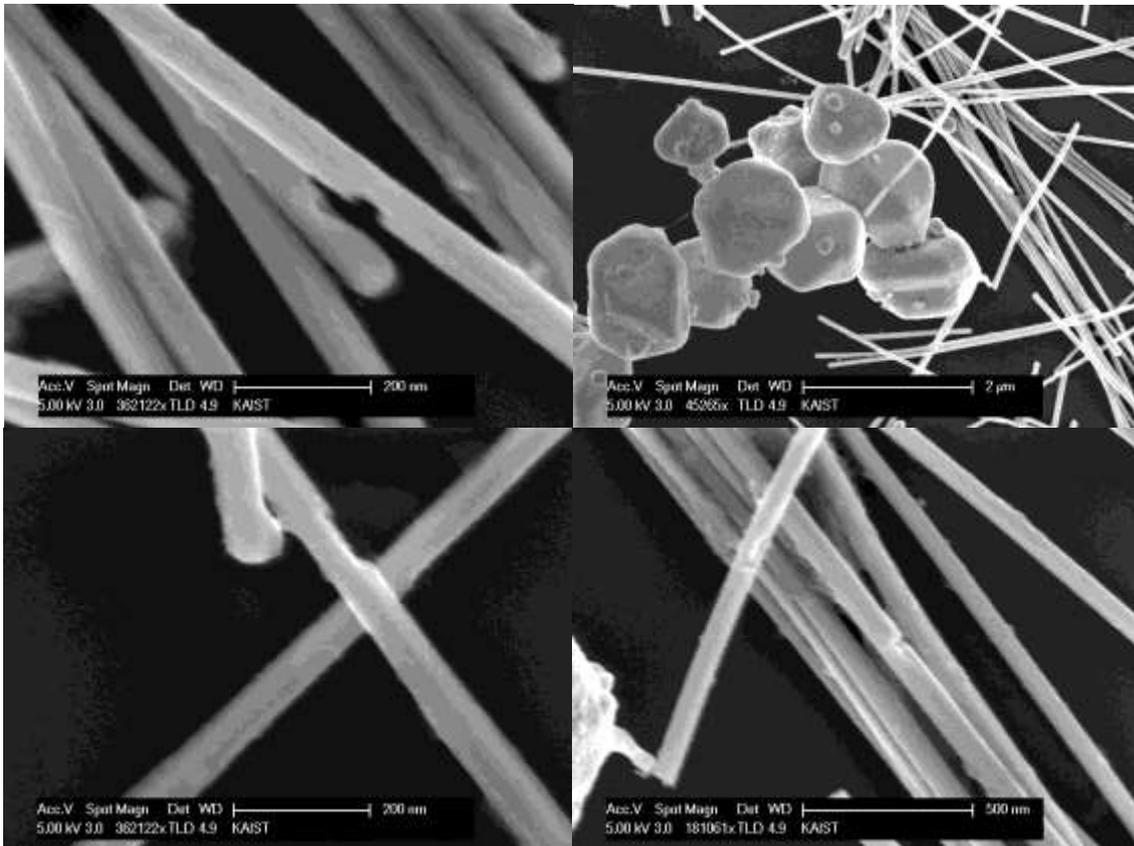
To confirm the existence of Au layer on the surface of the nanowire, cross-sectional selected area electron diffraction (SAED) of Au-coated Ag nanowire was collected using TEM-EDS as shown in Figure 4. The EDS clearly indicates that the Au is coated on the surface of the Ag nanowire homogeneously along the surface. Therefore, TEM analysis provided evidence that the  $[\text{Au}(\text{en})_2]\text{Cl}_3$  galvanic exchange coated the surface of the Ag nanowire with Au.



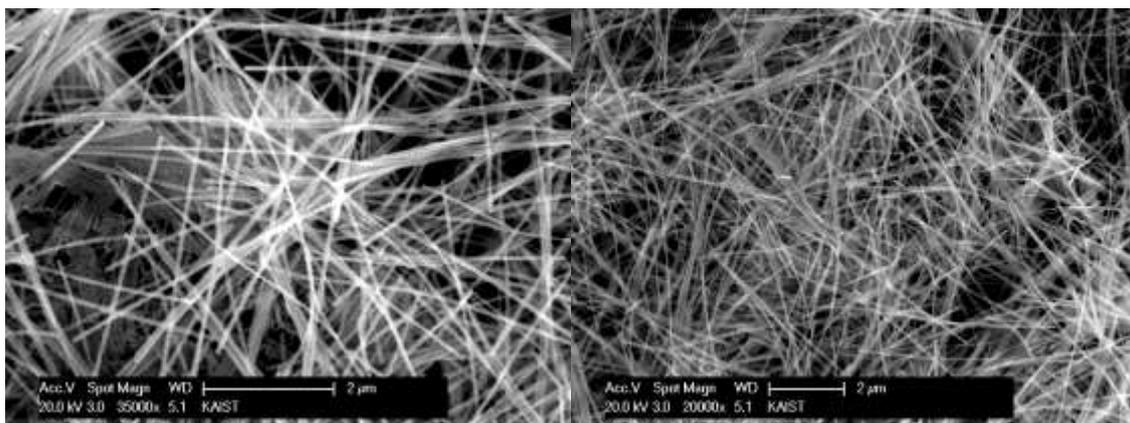
**Figure 4.** Cross-sectional SAED of Ag@Au nanowire and composition variation through the axis. Below is HRTEM image and XRD patterns of Ag@Au nanowire.

The morphology of the Pd(NO<sub>3</sub>)<sub>2</sub> exchanged nanowires is shown in the SEM images in Figure 5. Nanowires were truncated and partly deformed. There were some impurities as byproduct as well even though no AgCl formed. On the other hand, surface of [Pd(en)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> exchanged nanowires remained smooth, and the length distribution indicates that the length is preserved with an average of 12.5 μm, which is closer to the original length of 13.5 μm for the Ag nanowire batch synthesized for Pd coating. It was seen that mild oxidant help preservation of nanowire morphology to a great extent (Figure 6).

Coating Ag nanowires in solution opens up new possibilities to deposit as-synthesized core/shell nanowires onto the desired substrates at large scales. Thus the inert metal exchanged nanowires in methanol were electrostatically sprayed on polycarbonate or glass substrates and the optical properties were measured using the UV-vis spectrometer as shown in Figure 7 and 8. Also, influence of Pd coating was monitored by UV-vis spectrometer for two kinds of coatings as shown in Figure 9.



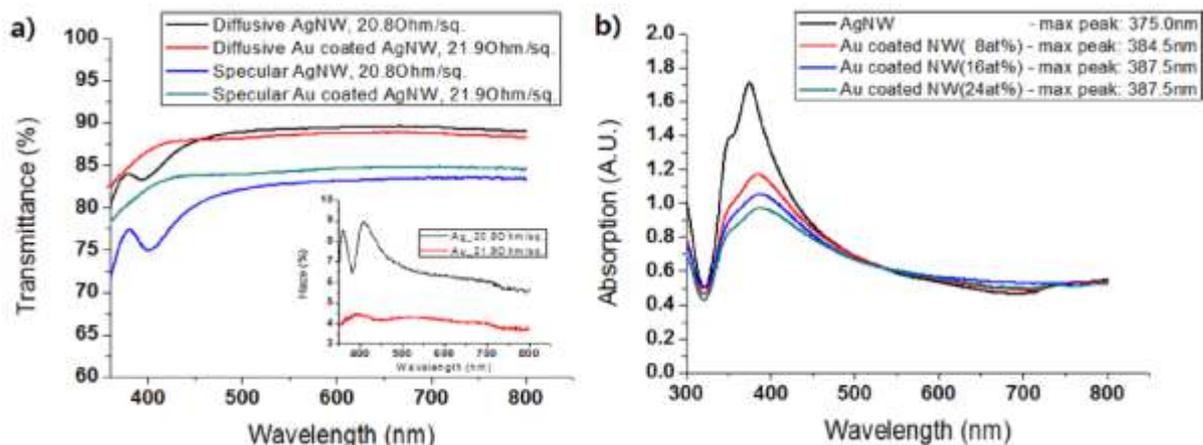
**Figure 5.** SEM images of Pd-coated Ag nanowires by  $\text{Pd}(\text{NO}_3)_2$  exchange.



**Figure 6.** SEM images of Pd-coated Ag nanowires  $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$  exchange.

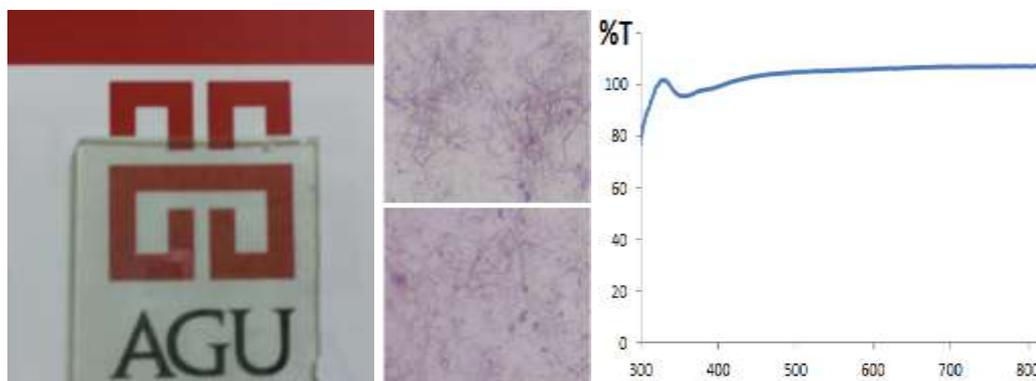
Within the visible light wavelength, Ag nanowire transparent electrode showed a plasmonic peak at wavelength of 375 nm, but this plasmonic peak was nearly extinct for the Au-exchanged Ag nanowire electrode. Reduced degree of scattering is apparent in the haze plot in Figure 7a inset that compared bare Ag nanowire electrode against the Au exchanged Ag nanowire electrode. The absorption spectrum in Figure 7b 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 studied for their difference in SPR frequency and absorbance.<sup>35</sup> In the work by Pal et al.,<sup>35</sup> 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  $[\text{Au}(\text{en})_2]\text{Cl}_3$  exchange has successfully altered the surface properties.

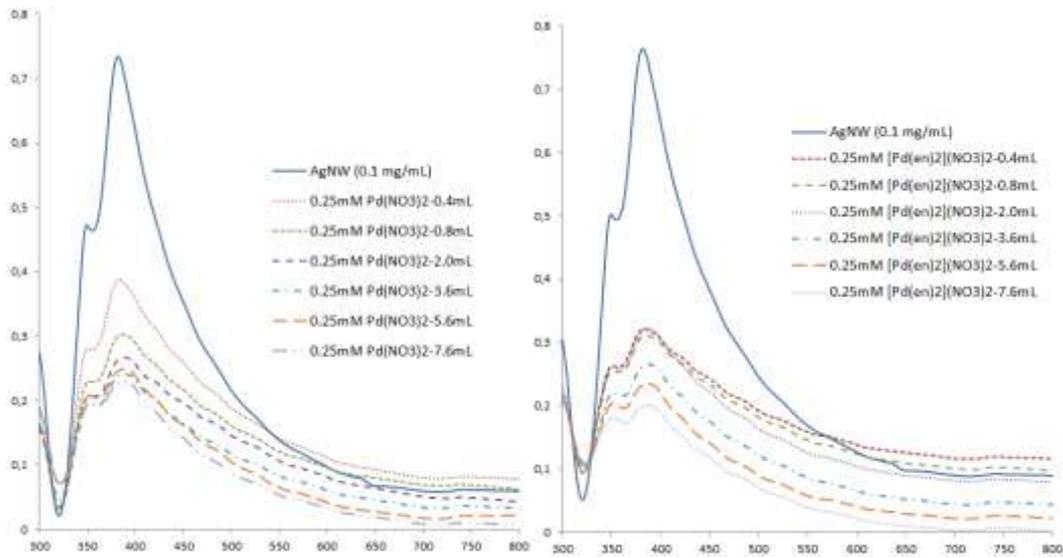


**Figure 7.** (a) Comparison of the UV-vis spectra of Ag nanowire films with sheet resistance of 20.8 Ohm/sq and the Au-coated Ag nanowire films with sheet resistance of 21.9 Ohm/sq. Inset: haze vs wavelength plot for Au-coated Ag nanowire films and Ag nanowire films. (b) Degradation of Ag SPR peak with increasing Au concentration from the galvanic exchange.

To our knowledge, for the first time in the literature, Pd coating was employed in order to design transparent electrodes for high transparency and strong chemical resistivity against nanowire oxidation. Storing Ag@Pd nanowire film deposited on polycarbonate substrate for 40 days altered the sheet resistance only by 10-15 Ohm/sq (Figure 8). UV-vis spectra of titrated Ag nanowire solutions showed that Ag plasmonic resonance peaks around 375 nm and 400 nm lose their intensity and shifts to the right slightly. This variation is also an indicator that the  $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$  exchange has successfully altered the surface properties (Figure 9). However, because Pd coated nanowires exhibit different adhesion property in methanol solvent than Ag nanowires, obtaining a more homogenous coating will be studied further with different kind of inks.

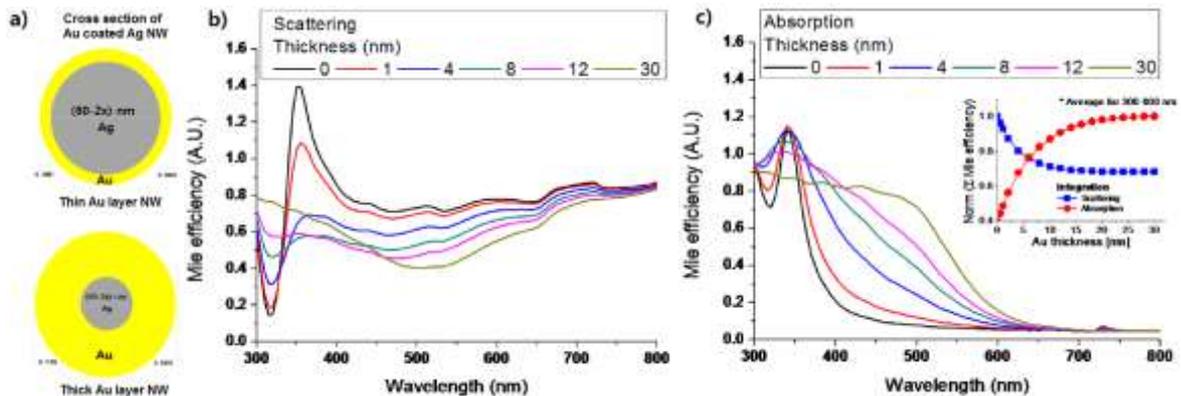


**Figure 8.** A picture of Ag@Pd nanowire film showing background through a glass substrate (left). Light microscope images of Ag@Pd nanowire films (middle). UV-vis spectrum of the same film showing an average transparency higher than 95% (right). Sheet resistance of the film was measured by 4-point probe is 176 Ohm/sq.



**Figure 9.** UV-vis spectra of Ag@Pd nanowires in aqueous solutions. The decrease of Ag nanowire SPR peak intensity and a slight shift to the longer wavelength can be seen.

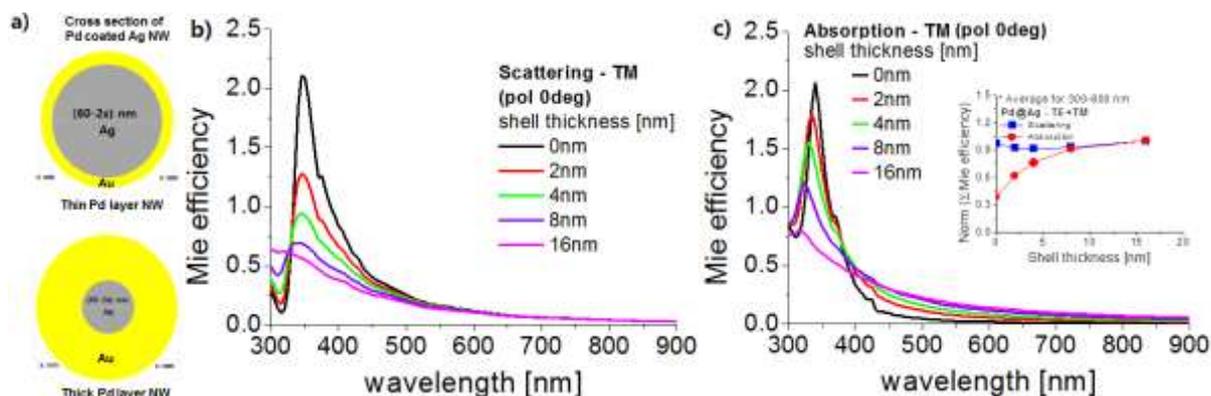
To provide insights to the mechanism for reduction in haze of inert metal-coated Ag nanowires, the optical properties of Au or Pd-coated Ag nanowire with different Au or Pd layer thicknesses were studied using the finite-difference time-domain (FDTD) simulations. The simulations employing 2D total field scattered field (TFSF) light source were performed in an air medium with mesh size of 0.3 nm. The optical constants of Ag, Au and Pd were acquired from literature<sup>25</sup> and the simulation results of TE and TM modes were averaged. An idealized case of the Ag nanowire with different Au or Pd layer thicknesses that were exchanged 1:1 with constant outer Au diameter was used for simplicity as illustrated in the schematic shown in Figure 10.



**Figure 10.** (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.

Light scattering for the Ag nanowires decreased with increasing Au layer thickness. However, the total absorption increased as shown in Figure 10b and c. Such trend is attributed to the difference in the basic optical properties of Ag and Au.<sup>36</sup> 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 10b, c). On the other hand, Au has relatively higher absorption and suppressed scattering characteristics compared to those of Ag (dark yellow lines in Figure 10b, c). Figure 10b 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 10c 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.



**Figure 11.** (a) Schematic illustration of varying thicknesses of Pd modeled in 2D FDTD simulations (b) scattering and (c) absorption over the wavelength 300–800 nm according to the Pd thickness obtained from the FDTD simulations in TM mode. Inset: normalized average scattering and absorption over the wavelength 300–800 nm according to the thickness of Pd layer (TE+TM mode).

Light scattering for the Ag nanowires decreased slightly with increasing layer thickness. However, the total absorption increased largely as shown in Figure 11c (inset). Such trend is attributed to the difference in the basic optical properties of Ag and Pd similar to that of Ag and Au case. Figures 10b and 10c show that the core-shell property becomes close to that of Pd as the shell thickness increases, and that effect is mostly saturated after the thickness of 8 nm is reached. Thus, thinner layer of Pd (1–4 nm) works better for haze reduction.

## CONCLUSION

In this study, inert metal galvanic exchanges using  $[\text{Au}(\text{en})_2]\text{Cl}_3$  and  $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$  were successfully used to coat the surface of the Ag nanowire with a thin layer of Au or Pd. The mild galvanic exchange reaction resulted in a slower reaction rate to only replace the outer surface with Au or Pd without truncating the Ag nanowires. Methanol suspensions of Au or Pd-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. Pd-coated Ag nanowire requires more working in order to obtain more homogeneous films with sheet resistance lower the found values of 175 Ohm/sq. It can be expected that less than 100 Ohm/sq sheet resistance is possible for Ag@Pd core/shell nanowire films. Ag@Pd core/shell nanowire films can be utilized as high surface area Pd catalyst in fuel cell systems and organic reactions. Transparency of the films may simplify and inspire new reaction systems that can be observed spectroscopy methods. Spectroelectrochemical studies can also benefit such systems to work with UV-vis and FTIR spectroscopy methods together with electrochemistry simultaneously.

Finally, inert metal layer can be used as an effective passivation layer against oxidation and sulfurization of Ag nanowires. Au or Pd-coated Ag nanowire electrode showed significantly smaller increase in sheet resistance after long time exposure to the air when compared to the Ag only nanowire electrode. Therefore, the outcomes of this study indicate that the Au or Pd-coated Ag nanowires can result in a low haze, chemically stable, and therefore, more reliable transparent electrode that can be applied to flexible displays or other electronics requiring high visibility.

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Notes

The authors declare no competing financial interest.

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