

Development of Highly Transparent Pd-Coated Ag Nanowire Electrode via Controlled Galvanic Displacement Reaction

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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. In our recent article, we demonstrated that coating Ag nanowires with a thin layer of Au through galvanic exchange reactions enhances the chemical stability of Ag nanowire films highly and also helps to obtain lower haze. In this study, coating of a thin Pd layer has been applied successfully onto the surface of Ag nanowires. A mild Pd complex oxidant $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$ was prepared in order to oxidize Ag atoms partially on the surface via galvanic displacement. The mild galvanic exchange allowed for a thin layer (1-2 nm) of Pd coating on the Ag nanowires with minimal truncation of the nanowire, where the average length and the diameter were 12.5 μm and 59 nm, respectively. The Pd-coated Ag nanowires were suspended in methanol and then electrostatically sprayed on flexible polycarbonate substrates. It has been revealed that average total transmittance remain around 95% within visible spectrum region (400-800 nm) whereas sheet resistance rises up to 175 Ohm/sq. To the best of our knowledge, for the first time in the literature, Pd coating was employed on Ag nanowires in order to design transparent electrodes for high transparency and strong chemical resistivity against nanowire oxidation. Very thin layer of Pd costs low, though this may render an excellent catalyst for applications such as fuel cell and organic synthesis.

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

1. Introduction

Transparent electrodes are of extensive scientific and technological interest as conducting layers in various optoelectronic devices. Specifically, the development of low-cost, flexible, transparent electrode materials exhibiting low sheet resistance ($R_s < 100 \text{ Ohm/sq}$) and high transmittance ($T = 90\%$) is crucial to realizing mechanically flexible displays, noninvasive biomedical devices, organic field-effect/light-emitting transistors (OFETs/OLETs), organic light emitting diodes (OLEDs) and photovoltaic cells (OPVs) [1,2]. Over the past few decades, indium tin oxide (ITO) has been the most popular material used for transparent electrodes [3,4]. However, ITO-based electrodes couldn't be applied to low-cost, flexible devices due to their several drawbacks such as mechanical brittleness, scarcity of indium resources, and high material and manufacturing costs. Furthermore, the necessity of high processing temperature (300–400 °C) to achieve sufficient conductance is a significant drawback for flexible optoelectronic applications employing polymer substrates. Therefore, considerable research efforts have focused on the development of alternative transparent electrode materials to replace ITO, which includes carbon nanotubes [5-7], graphene [8-10], and metal nanowires [11-14].

Among these alternative conductive materials, metal nanowires have recently attracted significant attention as transparent conductive electrodes due to their excellent optical and electrical properties. Recent studies have already indicated that the Ag nanowire network can surpass ITO with sheet resistance of lower than 100 Ohm/sq at an optical transparency of 90% [15,16]. In these studies, the Ag nanowires are typically synthesized in solution using the polyol reduction as previously done in our work [14]. The Ag nanowire films can preserve optical and electrical strength even after numerous bending, which makes it suitable for flexible devices [17,18]. Additionally, simplicity of large-scale spray-coating of Ag nanowires onto substrates of various materials and geometries made it possible to reduce ITO costs greatly.

For display applications, one of the major drawbacks of Ag nanowire films is high level of light scattering properties of Ag surface, which results in high haze (8-15%). This phenomenon is commonly attributed to the strong Surface Plasmon Resonance (SPR) effect of Ag. In our previous studies, we demonstrated that a thin layer of Au coating on Ag nanowires can be achieved via a relatively slow galvanic displacement reaction [19]. This coating layer altered the optical characteristics of Ag nanowires and resulted in reduced haze (from 8-15% to 2-4%), which is in the range of industrial requirements for flexible transparent electrodes. In addition, the chemical stability of Ag nanowire films were found to be significantly improved after Au coating. Heating at 80 °C in air for 2 weeks caused only a slight increase in the sheet resistance of the Ag@Au nanowire films whereas the sheet resistance of Ag nanowire films increased more than ten folds with the same treatment.

Motivated by our initial results obtained for galvanic displacement reactions of Au on Ag nanowires, in this study, we are interested in further exploring the thin-layer coating of Ag nanowires with a different metal, palladium (Pd). As the refractive indices and extinction coefficients of two metals are different, it can be expected to see reduced haze for Pd-coated Ag nanowire films while still keeping a high transparency (>90%). On the other hand, a higher chemical stability is expected for Ag@Pd core/shell nanowire films since Pd is more resistant against oxidation compared to Ag ($E_p[\text{Pd}^{2+}, 0.915 \text{ V}] > E_p[\text{Ag}^+, 0.800 \text{ V}]$). Although Pd coating on Ag nanowires is expected to reduce haze, a certain level of sheet resistance increase is also expected for Ag@Pd films compared to that of pristine Ag nanowire. This is mainly due to differences in bulk resistivity of Pd (105.4 nΩ·m) and Ag (15.87 nΩ·m) metals. Additionally, this new Ag@Pd core-shell system can render excellent

catalytic activities as a result of their high aspect ratios and they can reduce the cost of catalysis since a very thin layer (shell) requires little amount of Pd material. It's well known in the literature that palladium derivatives and Pd-based nanostructures can be used as catalysts in numerous chemical reactions and syntheses [20-22]. In particular, nanostructured palladium catalysts increase the rate and yield of the reactions significantly where surface area is a key function [21]. On the other hand, fuel cell catalysts with Pd content produce higher energy than those without Pd in it [23]. Formic acid fuel cells works well with Pd catalysts [24], which also contributes to recycling CO₂ and controlling its emission. Considering all these aforementioned issues, here we envision that new Ag@Pd core/shell nanowire films can be prepared for potential applications due to their easiness of the galvanic exchange process and spray-coating method may open up new possibilities for various applications.

2. Experimental procedure

2.1. Chemicals and Materials

Polyvinylpyrrolidone (PVP, $M_w \approx 40\ 000$, powder), silver nitrate (AgNO₃, 99.0%), and palladium(II) nitrate dihydrate (Pd(NO₃)₂, ~40% Pd basis) were purchased from Sigma-Aldrich. Sodium chloride (NaCl, 99.5%), potassium bromide (KBr, 99.0%), methyl alcohol (CH₃OH, 99.5%), ethylene glycol (EG, 99.0%), ethylene diamine, anhydrous (NH₂CH₂CH₂NH₂, 99.0%), and polycarbonate substrate (PC, average transmittance of 90%) were purchased from common commercial supplier. All chemicals were used without further purification.

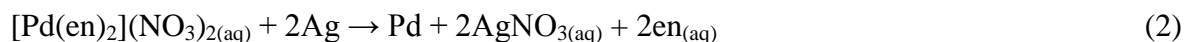
2.2. Synthesis of Pd-Coated Ag Nanowires

Ag nanowires were synthesized according to the polyol method described in our previous work.¹⁴ Density of the Ag nanowires dispersed in methanol was measured by weighing a measured volume of well-dispersed Ag nanowire solution after vacuum drying.

Pd coating was carried out using two different methods. In the first method (eq 1), the galvanic displacement reaction was carried out with 21.4 mL of 0.25 mM of Pd(NO₃)₂, which was titrated at a rate of 0.5 drops/s into the 50 mL solution of Ag nanowires in deionized water (density = 0.116 mg/mL). During the reaction, the stirring rate was 400 rpm. The pH of the Pd(II) solution was adjusted to 4.0 by addition of dilute nitric acid prior to the titration.



In the second method (eq. 2), a milder oxidizing complex, [Pd(en)₂](NO₃)_{2(aq)}, was first prepared in situ by mixing 1 equiv. of Pd(NO₃)_{2(aq)} with 4 equiv. of ethylenediamine(en)_(aq)(excess). Then, prior to the titration, the pH of the reaction solution was adjusted to 4.0 by adding dilute nitric acid. 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. Next, [Pd(en)₂](NO₃)_{2(aq)} (4.3 mL, 0.25 mM) was titrated at a 0.5 drop/s rate into the Ag nanowire dispersion solution while keeping the stirring rate at 400 rpm.



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.

2.3. Fabrication of Electrode

Electrostatic spray coating of the Pd-coated Ag nanowires was carried out as in our previous works [14,19]. Pd@Ag 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 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.

2.4. Nanowire Electrode Characterization

Transmittance of the electrostatically sprayed 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 Pd-coated Ag nanowires were imaged using a scanning electron microscope (SEM) (Stereoscan S440, Leo), and the average composition of 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 Pd-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 $\text{HCl}_{(\text{aq})}$ 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 $\text{NaOH}_{(\text{aq})}$. 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.

3. Results and discussion

A thin layer of Pd on Ag nanowire surface is expected to scatter light less than Ag nanowire itself due to weaker surface plasmon resonance (SPR), and also smaller average ratio of refractive indices relative to that of air along visible spectrum, e.g. $n_{\text{Air}}=1.000$, $n_{\text{Pd}}=1.695$, $n_{\text{Ag}}=0.121$ at $\lambda=589.29$ nm. When a film of 4.0 nm thickness for both metals are tested to observe reflectance (R) between $75^\circ > \theta > 15^\circ$ angle of incidence, results are significantly different, $0.714 > R_{\text{Pd}} > 0.674$ and $0.967 > R_{\text{Ag}} > 0.962$ ($\lambda=589.29$ nm, film

thickness=4.0 nm), whereas extinction coefficients(k) and absorbance(α) values are closer ($k_{Ag}=4.06$, $\alpha_{Ag}=8.66 \times 10^5$ and $k_{Pd}=3.65$, $\alpha_{Pd}=7.79 \times 10^5$ where $\lambda=589.29$ nm, film thickness=4.0 nm) [25]. 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_2O or Ag_2S [26]. Therefore, a thin Pd coating layer 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.

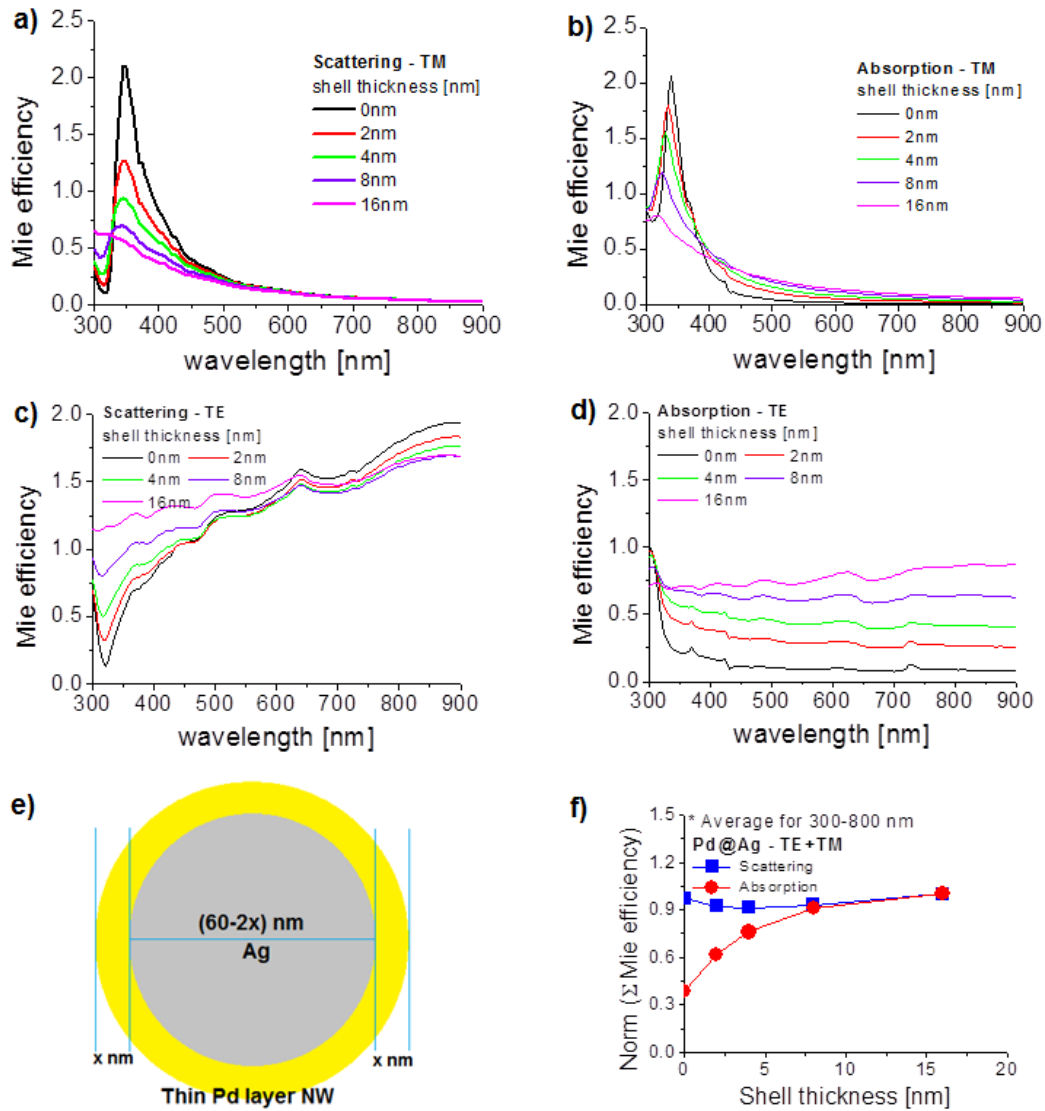


Fig. 1. Schematic illustration of varying thicknesses of Pd modeled in 2D FDTD simulations in (e). (a) Scattering and (b) absorption over the wavelength 300–900 nm according to the Pd thickness obtained from the FDTD simulations in TM mode, (c) and (d) in TE mode. (f) Normalized average scattering and absorption (TE+TM mode).

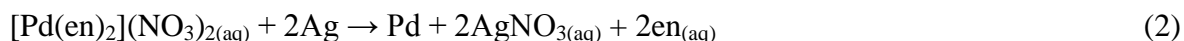
Prior to the synthesis of new Pd-coated Ag nanowires, we performed computational analysis on our new core-shell nanowire system to reveal the optimum coating layer thickness and to gain insights into the mechanism of haze reduction. The optical properties of Pd-coated Ag nanowire with different Pd layer 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 0.5 nm. The optical constants of Ag and Pd were acquired from literature [25]. An idealized case of the Ag nanowire with different Pd layer thicknesses that were exchanged 1:1 with constant outer diameter was used for simplicity as illustrated in the schematic shown in Fig. 1.

The simulation results for scattering and absorption property of core-shell structures in TE and TM modes are shown in Fig. 1a-d. And the integrated (TE+TM) value over 300 – 800 nm range were normalized and they are shown in Fig. 1f. As expected, light scattering for the Ag nanowires decreased with increasing Pd layer thickness. However, the total absorption increased. Such trend is attributed to the difference in the basic optical properties of Ag and Pd similar to that of Ag and Au case [19]. Fig. 1b, d show that the amount of reduced peak absorption by increasing shell thickness is smaller than the increase of absorption in longer wavelength. Therefore, the overall absorption of core-shell structure increases as the shell thickness increases as shown in Fig. 1f. Fig. 1 shows 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 for average influence. FDTD simulations indicate that the 3-4 nm thickness of Pd layer is optimal for scatter reduction while still keeping a relatively low absorption. Thus, thinner layer of Pd (3-4 nm) works better for the optimal balance of haze and transparency.

The full galvanic exchange of Ag nanowire with Au, Pt and Pd was demonstrated in the literature in order to make nanoshells [27,28]. In these reactions, since the reduction potential of Pd(II) species are higher than that of Ag(I), reaction proceeds to the side where Ag dissolves and Pd precipitates on the surface. Two Ag atoms are replaced by one Pd atom. During these galvanic exchange reactions, if a chloride compound of an inert metal is used, AgCl precipitate forms when the concentration reaches a critical value. Therefore, a non-chloride compound ($\text{Pd}(\text{NO}_3)_2$) was used in this study to prevent the precipitation of AgCl. Galvanic exchange reactions proceed at high rates when a large potential difference drives the reaction. However, high rate of electrochemical reactions may cause truncation of nanowires resulting in the destruction of layer thickness and the formation of undesired surface morphologies.

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 high formation constants ($\log \beta > 20$) [29]. Diamines coordinate to Pd(II) cation through both amino groups, forming stable five-membered chelate ring. Extra stabilization of the complexes lowers the reduction potentials to a great extent.



Here, the reduction potential for $[\text{Pd}(\text{en})_2]^{2+}/\text{Pd}^0$ is smaller than that of the $\text{Pd}^{2+}/\text{Pd}^0$ because (en) ligand stabilizes the Pd^{2+} oxidation state against reduction [30-33]. Although $[\text{Pd}(\text{en})_2]^{2+}$ complexes were synthesized and isolated as single-crystals in the literature, to the best of our knowledge their reduction potentials are not reported [34]. In the work by Zhu et al. [30], the difference of reduction potentials between $[\text{Au}(\text{en})_2]^{3+}/\text{Au}^0$ and $\text{AuCl}_4^-/\text{Au}^0$ was -0.7 V ($E_p[\text{AuCl}_4^-], 0.410 \text{ V} > E_p[\text{Au}(\text{en})\text{Cl}_2^+], 0.140 \text{ V} > E_p[\text{Au}(\text{en})_2^{3+}], -0.290 \text{ V}$) and a similar reduction potential shift is also expected between eqs 1 and 2. For instance, for a Pd(II) complex with $\log \beta=20$, new reduction potential, $E_p[\text{Pd}(\text{II}) \text{ complex}]$ would be 0.324

V at standard conditions. The difference can be found via Nernst Equation as follows:

$$E = E^0 - 2.303RT(\log \beta)/nF$$

$$\Delta E = E - E^0 = -2.303RT(\log \beta)/nF$$

$$\Delta E = -2.303 * 8.314 * 298 * 20/2 * 96485 = -0.591 \text{ V}$$

Prior to addition of chelating agent (ethylenediamine), pH (~4.0) of the solution was kept as low as possible in order to prevent the formation of insoluble hydroxide species [29]. Even so, Pd ratio in the core/shell nanowire composition indicates that Pd complex reacts only partially so that Pd ratio is lower than planned. A planned 8% exchange reaction results in only around 3.1% of Pd in the composition. The main objective of this study is to use milder reaction conditions to coat only the outer surface of the Ag nanowire with an inert metal, and the thickness of the inert metal layer can be controlled by the concentration of the complex in the solution (Fig. 2).

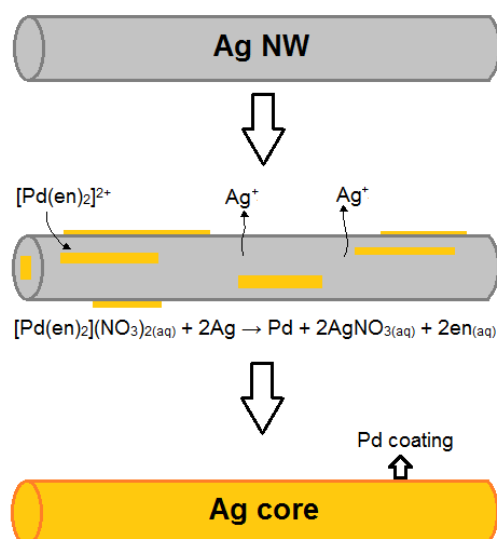


Fig. 2. Schematical representation of Pd-coating on the Ag nanowire through a galvanic displacement reaction.

The SEM-EDS results shown in Fig. 3 showed that nanowire lengths were preserved due to little truncation with mild oxidation. Nanowire surfaces look smooth in the images. This is evidence to homogeneous coating of nanowires. The overall composition from the galvanic displacement reaction is 3.1 at.% for Ag@Pd nanowire. This composition will result in coating thickness of 0.40 nm for Pd coating. Layer thickness was roughly calculated by a formulation derived for cylindrical core/shell system (Fig. 3). Number of atoms (N_{atom}) were taken from EDS result, $R_{\text{Ag}}=144.5 \text{ pm}$, $R_{\text{Pd}}=137.0 \text{ pm}$. The formulation was described in our previous work in detail.¹⁹

The morphology of the Pd(NO₃)₂ exchanged nanowires is shown in the SEM images in Fig. 4. 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)₂](NO₃)₂ 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 (Fig. 5).

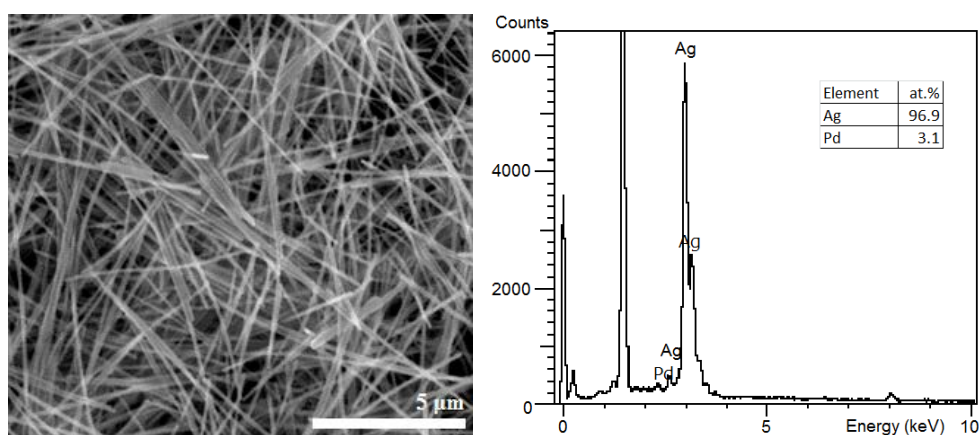


Fig. 3. SEM image of Pd@Ag core-shell nanowires (left) and SEM-EDS data for Pd and Ag (right).

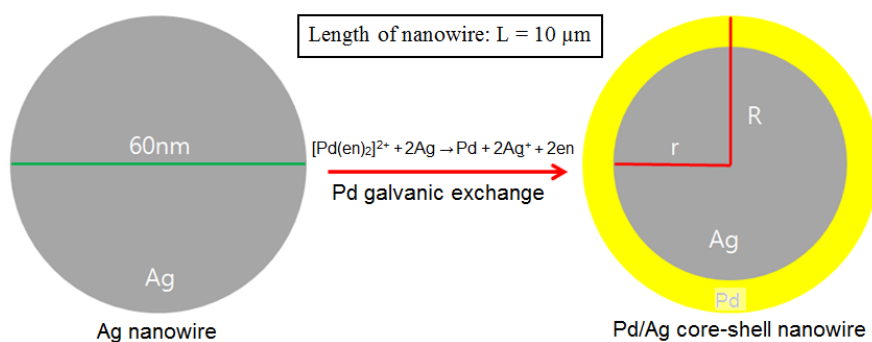


Fig. 4. Schematic for the cross section of Ag nanowire before and after Pd galvanic exchange.

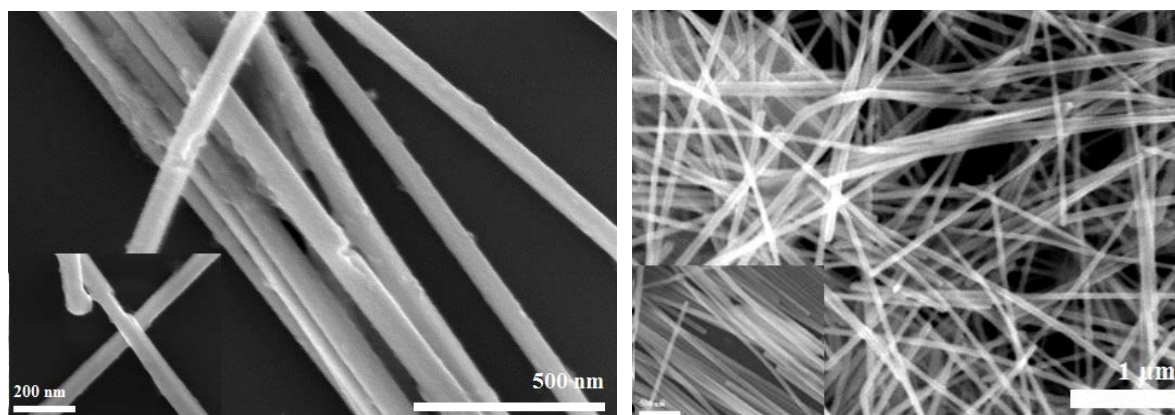


Fig. 5. SEM images of Pd-coated Ag nanowires by $\text{Pd}(\text{NO}_3)_2$ exchange (Left). SEM images of Pd-coated Ag nanowires $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$ exchange (Right).

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 substrates and the optical properties were measured using the UV-vis spectrometer as shown in Fig. 7. Also, influence of Pd coating was monitored by UV-vis spectrometer for two kinds of coatings as shown in Fig. 8.

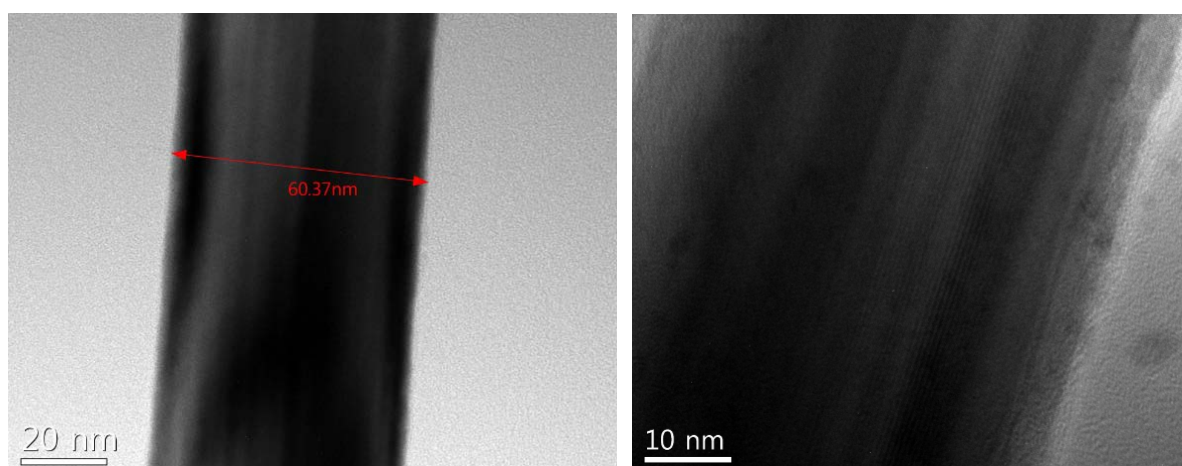


Fig. 6. TEM and HRTEM images of Pd@Ag core/shell nanowires by $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$ exchange. Uniformity of coating and well-ordered crystallinity can be noted.

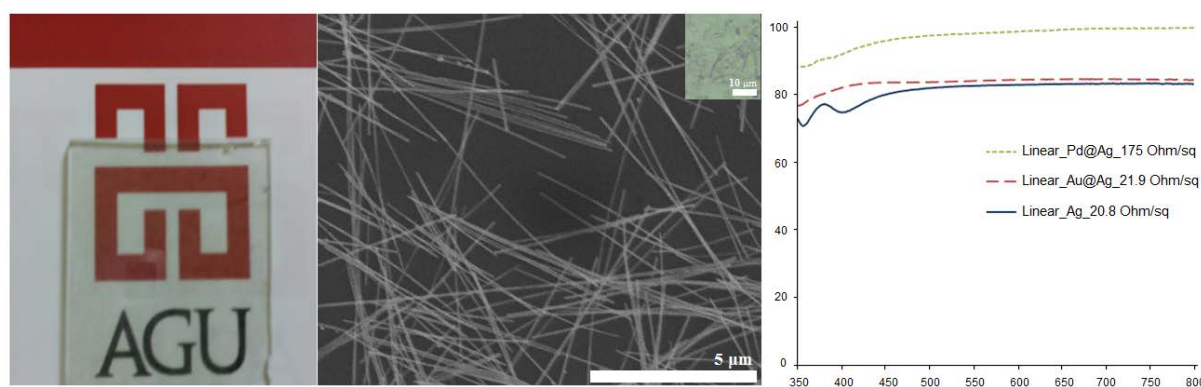


Fig. 7. A picture of Ag@Pd nanowire film showing background through a polycarbonate substrate (left). SEM images and light microscope images (inset) of Ag@Pd nanowire films (middle). UV-vis spectrum of the same film showing an average transparency higher than 95% and a haze ratio $\sim 1.9\%$ (right). Sheet resistance of the film was measured by 4-point probe is 175 Ohm/sq. For comparison, UV-vis spectra of Ag nanowire film (sheet resistance: 21.9 Ohm/sq) and Au@Ag nanowire film (sheet resistance: 20.8 Ohm/sq) from previous work was plotted together.

Within the visible light wavelength, Ag nanowire transparent electrode showed two plasmonic peaks at wavelengths of 375 nm and 400 nm, but these plasmonic peaks were shorter for the Pd-exchanged Ag nanowire electrode. The absorption spectrum in Fig. 8 for different degrees of Pd 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 Pd concentration. The variation in the Ag plasmonic resonance peak is also an indicator that the $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$ exchange has successfully altered the surface properties. Ag@Pd nanotubes have been studied for their catalytic application in fuel cells [27]. In the work by Jiang et al. [27], the authors also show that the composition of the Ag@Pd core/shell nanowires and nanotubes can result in a SPR peak shift at the red side of the spectrum. Storing Ag@Pd nanowire film deposited on polycarbonate substrate for 13 days in air under 80 °C altered the sheet resistance only by a few Ohm/sq (175 Ohm/sq \rightarrow 182 Ohm/sq) (Fig. 9). However, since Pd-coated nanowires exhibit different adhesion property in methanol solvent than Ag nanowires do, obtaining a more homogenous coating needs to be studied further with

different kind of inks (Fig. 7). To the best of our knowledge, for the first time in the literature, Pd coating was employed on Ag nanowires in order to design transparent electrodes for high transparency and strong chemical resistivity against nanowire oxidation.

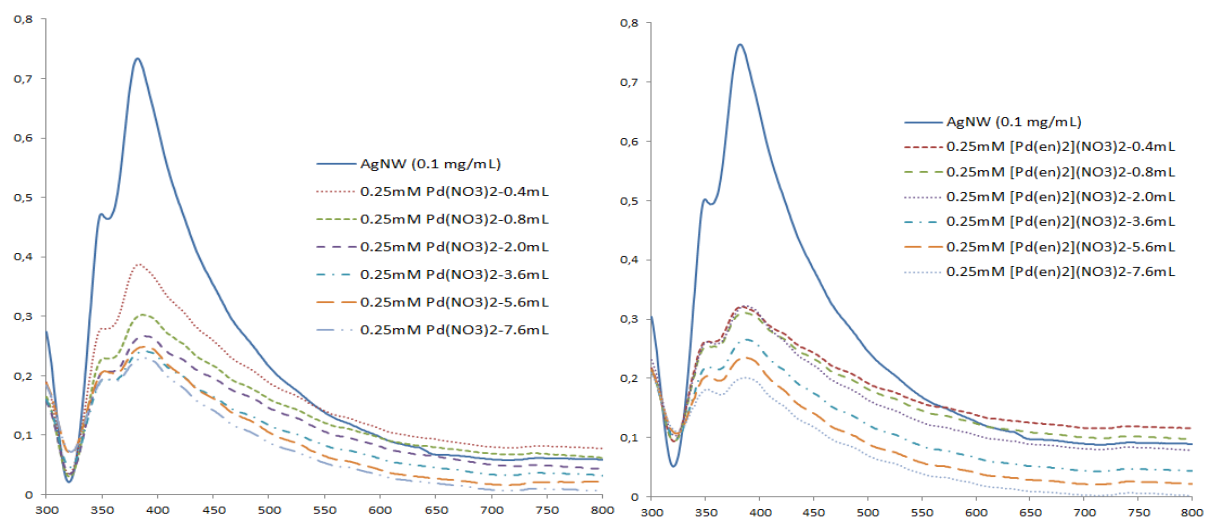


Fig. 8. UV-vis spectra of Ag@Pd nanowires in aqueous solutions. The decrease of Ag nanowire SPR peak intensity and a slight shift to the longer wavelength can be seen.

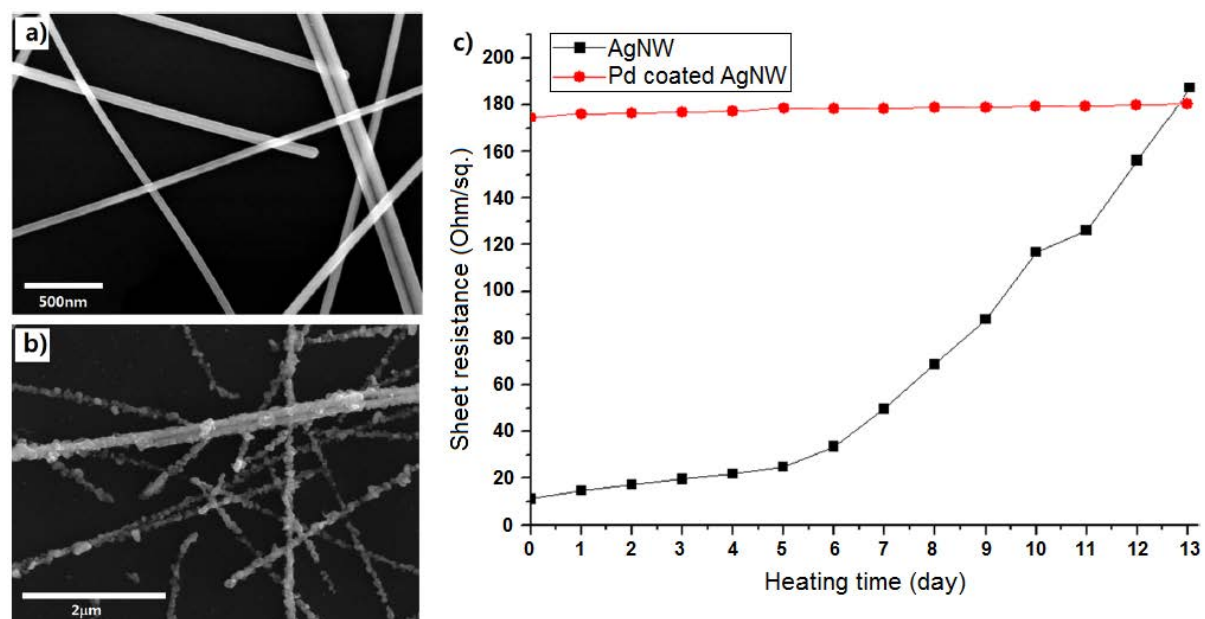


Fig. 9. (a) SEM images of the Ag nanowire electrode before and (b) after 17 days heating at 80 °C in air from our previous work [19]. (c) Elevation of the sheet resistance and comparison of the Ag nanowire and Pd-coated Ag nanowire electrode performance when heated at 80 °C in air.

4. Conclusions

In this study, inert metal galvanic exchanges using $[\text{Pd}(\text{en})_2](\text{NO}_3)_2$ were successfully used to coat the surface of the Ag nanowire with a thin layer of Pd. The mild galvanic exchange reaction resulted in a slower reaction rate to only replace the outer surface with Pd without truncating the Ag nanowires. Methanol suspensions of Pd-coated Ag nanowires were

electrostatically deposited on polycarbonate substrate and evaluated for the electrical, optical properties. Total transmittance for the case of Pd-coated Ag nanowire with average concentration of 3.1 at.% Pd was around 95% and the haze was 1.9%. The presence of the Pd layer resulted in reduction and red-shift of the Ag plasmonic peak, and the FDTD simulations confirmed that the exchange of Ag with Pd outer surface can result in significant reduction in scattering and haze. Pd-coated Ag nanowire requires more working in order to obtain more homogeneously textured films with sheet resistance lower than 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 as well. Transparency of the films may simplify and inspire new reaction systems that can be observed with 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. 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 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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