

Synthesis of Cu–Ag, Cu–Au, and Cu–Pt Core–Shell Nanowires and Their Use in Transparent Conducting Films

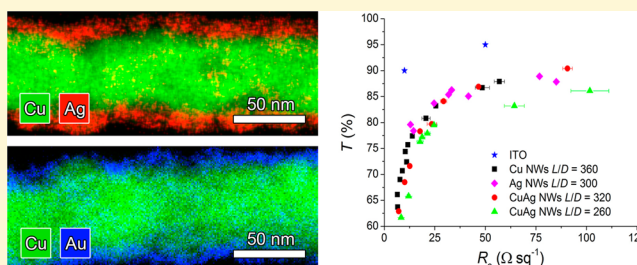
Ian E. Stewart,[†] Shengrong Ye,[†] Zuofeng Chen,[‡] Patrick F. Flowers,[†] and Benjamin J. Wiley^{*,†}

[†]Department of Chemistry, Duke University, 124 Science Drive, Box 90354, Durham, North Carolina 27708, United States

[‡]Department of Chemistry, Tongji University, Shanghai 200092, China

S Supporting Information

ABSTRACT: This article describes a room-temperature solution-phase process for the synthesis of copper–silver (Cu–Ag), copper–gold (Cu–Au), and copper–platinum (Cu–Pt) core–shell nanowires (NWs) in which ascorbic acid removes the passivating copper oxide coating from the Cu NWs and reduces noble metal ions onto the Cu NWs while preventing galvanic replacement. Cu–Ag NWs are conductive as printed, and the resulting NW films exhibit optoelectronic properties equivalent to films of Ag NWs with a similar aspect ratio. Unlike Cu NWs, Cu–Ag NWs were resistant to oxidation in dry air at 160 °C and under humid conditions (85% RH) at 85 °C for 24 h.



1. INTRODUCTION

Transparent conductors (TCs) are necessary components for smartphones, organic photovoltaics (OPVs), perovskite solar cells (PSCs), organic light emitting diodes (OLEDs), flat panel displays, and touch sensors. Indium tin oxide (ITO) is the most common material used for TCs due to its low sheet resistance ($R_s = 10 \Omega \text{ sq}^{-1}$) and high visible light transmittance (>90% T).¹ However, the high-conductivity ITO used in large-area touch screens, OPVs, PSCs, and OLEDs is particularly costly due to the slow linear coating rates involved with the vapor phase deposition of relatively thick ITO films.² Since solution-phase coating processes do not have to sacrifice speed for thickness and offer coating speeds more than 100-times faster than sputtering methods, an ITO alternative that could be coated from solution without compromising performance would reduce the cost of OPVs, PSCs, and OLEDs.

Proposed replacements for ITO include carbon nanotubes (CNTs),^{3,4} graphene,^{5,6} and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS),^{7,8} but only metal nanowires are both solution-coatable and demonstrate performance comparable to ITO.^{9,10} Silver nanowires (Ag NWs) have become the most promising ITO alternative as they are conductive after coating. Copper on the other hand is only 6% less conductive than silver ($\rho_{\text{Cu}} = 1.68 \times 10^{-8} \Omega \text{ m}$, $\rho_{\text{Ag}} = 1.59 \times 10^{-8} \Omega \text{ m}$) but is more than 100-times cheaper and 1000-times more abundant.¹¹ These factors make copper nanowires (Cu NWs) an enticing alternative to Ag NWs, but there are still factors limiting their widespread use. Cu NW films are insulating after printing from an ink due to the formation of copper oxides on the surface of the NWs. Annealing under hydrogen at 175 °C can reduce the surface oxides and sinter the NWs together to render the films conductive,^{10,12} but this method is not convenient and does not

inhibit future copper oxidation. Low-temperature solution-based approaches were recently shown to produce similar optoelectronic performance for Cu NW films as H₂ gas annealing by selectively dissolving the copper oxides with acetic acid, but this method does not protect the NWs from corrosion.^{13–15} There have been numerous efforts to prevent Cu NW oxidation including encapsulating the Cu NWs in shells of Ni,^{13,16} Zn, Sn, In,¹⁷ graphene,¹⁸ aluminum-doped zinc oxide (AZO),¹⁹ or embedding the NWs in a plastic.²⁰ However, there is as yet no method that enables Cu NWs to be conductive as printed and protects them from oxidation in a single step, and thereby solves the major disadvantage of Cu NWs relative to Ag NWs. For Cu NWs to be competitive, a user has to be able to simply coat them from solution to get a conductive film that is resistant to oxidation with no extra steps, just as is the case for Ag NWs.

In this work, we show that a thin shell of silver can be electrolessly deposited on Cu NWs to confer oxidation resistance and conductivity to the resulting NW films immediately after they are printed with no postprocessing. Nanoscale deposition of less active metals onto more active metals, such as gold onto silver^{21,22} or silver onto copper,^{23,24} typically proceeds through galvanic replacement, which corrodes and oxidizes the metal template.^{25,26} Yang et al.²² demonstrated that a gold shell can be deposited onto silver nanocubes without galvanic etching of the silver by using ascorbic acid in an alkaline solution. By increasing the concentration of the reducing agent, we were able to eliminate the basic conditions, suppress the galvanic replacement of

Received: September 21, 2015

Revised: November 2, 2015

Published: November 4, 2015

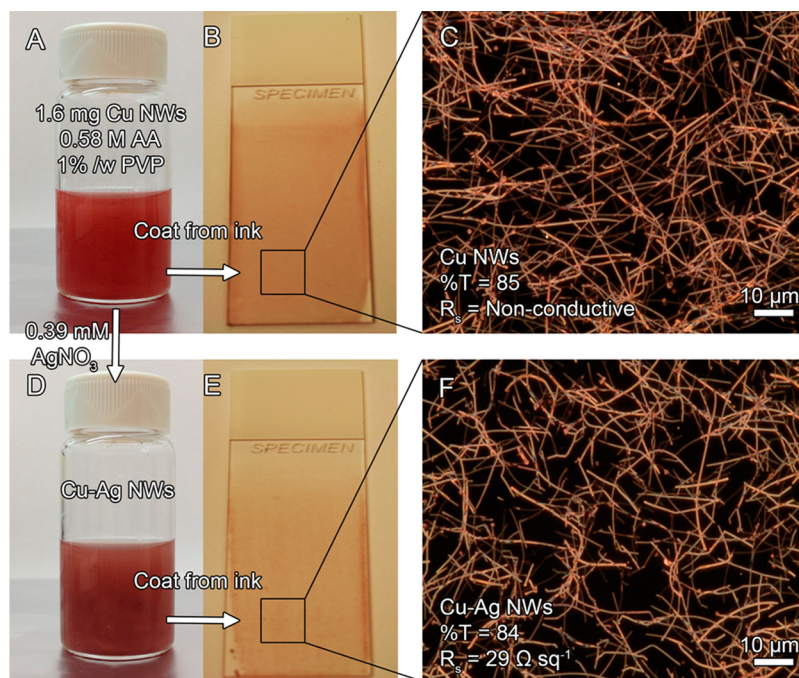


Figure 1. (A) A vial containing the Cu NWs suspended in a solution of ascorbic acid (AA) and PVP. (B) A film of Cu NWs coated via Meyer rod from an ink. (C) DFOM image of a Cu NW network at 85% T. (D) A solution of Cu–Ag NWs after 0.39 mM AgNO_3 was added to the solution in panel A. (E) A film of the Cu–Ag NWs coated from ink. (F) DFOM image of a Cu–Ag NW network that is conductive after coating.

copper by silver, and induce silver reduction onto Cu NWs. The resulting films of Cu–Ag core–shell NWs are as conductive and oxidation resistant as pure Ag NWs. We further show how the same synthetic approach can be used to make Cu–Au and Cu–Pt core–shell NWs.

2. EXPERIMENTAL SECTION

2.1. Nanowire Synthesis. 2.1.1. Copper Nanowire Synthesis.

Cu NWs ($L = 28 \pm 10 \mu\text{m}$ and $D = 79 \pm 22 \text{ nm}$) were donated by NanoForge Corp.¹² The NWs were stored in an aqueous polyvinylpyrrolidone (PVP, MW = 10 kDa, 1% by weight, Aldrich) and diethylhydroxylamine (DEHA, 3% by weight, Aldrich) solution (PVP/DEHA) with a final concentration of 0.8 mg/mL of NWs.

2.1.2. Silver Nanowire Synthesis. Ag NWs ($L = 15 \pm 3 \mu\text{m}$ and $D = 63 \pm 7 \text{ nm}$) were synthesized according to the polyol method^{27,28} and stored in isopropanol (IPA, BDH). First, 158.4 mL of ethylene glycol (EG, J.T. Baker analyzed reagent grade) was heated at 130 °C with an oil bath in a stoppered 500 mL round-bottom flask for 1 h. Four solutions were then prepared: (1) 0.257 g of NaCl in 20 mL of EG, (2) 0.081 g of $\text{Fe}(\text{NO}_3)_3$ in 10 mL of EG, 1.05 g of PVP (MW = 55 kDa) in 25 mL of EG, and (4) 1.05 g of AgNO_3 in 25 mL of EG. Next, 0.2 mL of solution (1), 0.1 mL of solution (2), 20.76 mL of solution (3), and 20.76 mL of solution (4) were added to the preheated 500 mL flask in that order with about 30 s between each addition. The flask was then stoppered, and the reaction was allowed to proceed at 130 °C for 7 h. The Ag NWs were then purified with water and stored in IPA.

2.1.3. Copper–Silver/Gold/Platinum Nanowire Synthesis. A 20 mL scintillation vial was filled with 2 mL of the Cu NWs in the PVP/DEHA storage solution mentioned earlier, 5.5 mL of 1 M ascorbic acid (Alfa Aesar), and 2 mL of 5 wt % PVP in DI water. This solution was stirred rapidly for 3 min. To produce Cu–Ag NWs with 5 and 15 nm thick shells of silver, 0.15 and 0.5 mL of 0.025 M AgNO_3 (Carolina Biological Supply Company), respectively, were added with a pipet in <1 s to the scintillation vial, and the contents were left stirring for ~2–3 min. The Cu–Ag NW solution was then briefly and lightly vortexed to remove any aggregation. This procedure was the same for making Cu–Au and Cu–Pt NWs, except 0.075 mL of 0.025 M of HAuCl_4

(Aldrich) and 0.947 mL of 0.01 M K_2PtCl_6 (Aldrich) were used, respectively, instead of AgNO_3 .

2.2. Nanowire Film Fabrication. Prior to preparing the transparent electrodes, the glass substrates (7.62 cm \times 2.54 cm microscope slides, VWR) were sonicated in acetone for 10 min and transferred to IPA to remove surface contaminants. The slides were wiped dry with a kimwipe and blown with air prior to NW deposition.

2.2.1. Copper Nanowire Film Fabrication. The Cu NWs in PVP/DEHA storage solution were collected into a 1.5 mL vial, centrifuged, and the supernatant was removed. Next, the NWs were washed three times with 1 mL of 3 wt % DEHA, once with 1 mL of 190 proof ethanol (Koptec), and once with 1 mL of an ink formulation (0.06 g nitrocellulose (Scientific Polymer) dissolved in 2.94 g of acetone (EMD) with subsequent addition of 3 g of ethanol (Koptec), 0.5 g of ethyl acetate (Aldrich), 1 g of pentyl acetate (Aldrich), 1 g of IPA, and 1.7 g of toluene (Aldrich)). The suspensions were vortexed between each wash.

Following removal of the ink wash supernatant, a small amount of the ink was added to the NWs. This suspension was vortexed to disperse the NWs in the ink, and 35 μL was pipetted in a line across the top of the glass slide. A Meyer rod (Gardco #13) was then quickly (<1 s) drawn down the slide by hand to evenly spread the NW coating. The amount of ink added to the NWs could be varied to alter the transmittance and sheet resistance of the final film. The Cu NW films were not immediately conductive after coating. To remove the remaining nitrocellulose and sinter the NWs together, the Cu NW films were plasma cleaned in a forming gas (95% N_2 , 5% H_2) atmosphere for 2 min and then placed in a tube furnace at 200 °C for 30 min under a constant flow of H_2 (600 mL min^{-1}).

2.2.2. Silver Nanowire Film Fabrication. The Ag NWs were first decanted from the IPA storage solution after centrifugation. They were then similarly washed with 1 mL of the nitrocellulose ink formulation and coated via Meyer rod from this ink. The Ag NW films were conductive after washing with acetone for 30 s (repeated twice) and DI water for 60 s.

2.2.3. Copper–Silver/Gold/Platinum Nanowire Film Fabrication. The Cu–Ag, Cu–Au, and Cu–Pt NWs were collected by centrifuging the reaction solution in Section 2.1.3 at 2000 rpm for 2 min until the NWs settled and the supernatant could be removed. The NWs were

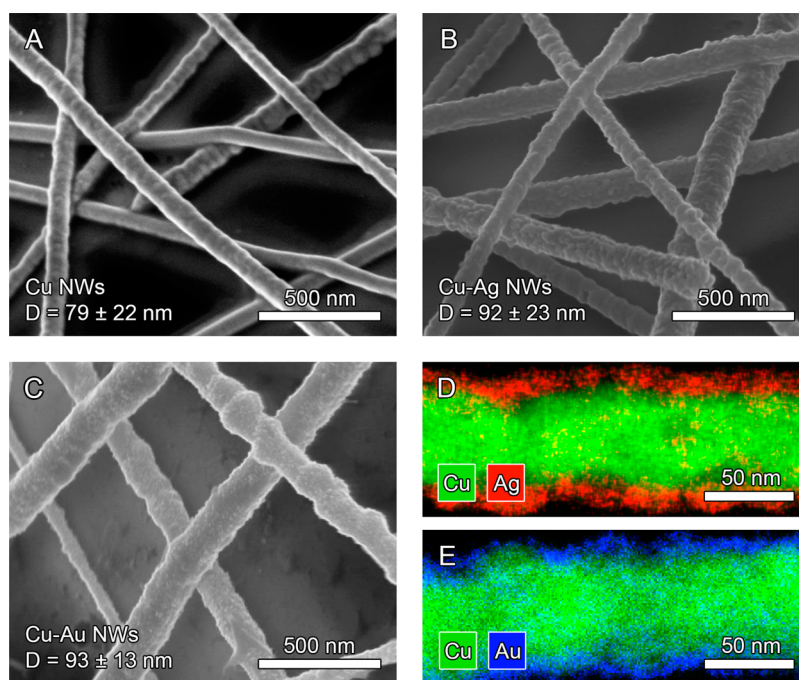


Figure 2. SEM images of (A) Cu NWs, (B) Cu–Ag core–shell NWs, and (C) Cu–Au core–shell NWs. Average diameters were calculated from 50 distinct nanowires. (D, E) TEM–EDS images of Cu–Ag and Cu–Au NWs.

then washed twice at 2000 rpm for 2 min with 1.5 mL of 190-proof ethanol to remove the ascorbic acid and PVP, and once with 1.5 mL of the ink formulation at 2000 rpm for 3 min. The solutions were briefly vortexed (<5 s) between washing steps.

Films of Cu–Ag, Cu–Au, and Cu–Pt NWs were conductive immediately after coating, but a 30 s acetone rinse (repeated twice) and a 60 s water rinse (with air drying under an air knife between each rinse) could be performed to remove the nitrocellulose and any remaining PVP to increase the transparency of the films.

2.3. Hollow Nanowire Experiments. Films of Cu NWs were fabricated as mentioned earlier. These films were then dipped in acetone or 0.58 M ascorbic acid for 2×30 s and 3×10 s, respectively, to produce the desired film of Cu NWs and dried under N_2 gas from an air knife. Once dry, the films were immersed in 20 mL of 0.025 M $AgNO_3$ for 2 min to produce hollow NWs. To obtain SEM images of the nanowire films, the NWs were scraped off the glass slides via a razor blade, concentrated in IPA, sonicated for 1 min, pipetted onto a silicon SEM wafer (Silicon Wafer International), and allowed to dry prior to SEM characterization. For hollow gold and platinum NWs, the above procedure involving immersing a Cu NW film in 0.58 M ascorbic acid was repeated with 0.025 M $HAuCl_4$ and 0.005 M K_2PtCl_6 .

2.4. Oxidation Resistance. Dry oven sheet resistance (R_s) measurements were periodically taken with a four-point probe. Humidity chamber measurements were taken by first cutting the NW films into $1 \text{ cm} \times 2.54 \text{ cm}$ pieces then defining a $1 \text{ cm} \times 1 \text{ cm}$ area with silver paste and finally placing the samples in a Test Equity 200H Series Temperature/Humidity Chamber at $85^\circ\text{C}/85\% \text{ RH}$. Sheet resistance measurements were made by wiring connections from the silver paste ends on the samples to a multimeter through a port on the humidity chamber. Each time point is an average of five multimeter measurements.

2.5. Instrumentation and Characterization. Dark field optical microscopy (DFOM) images were taken with an Olympus BX51 microscope. SEM (FEI XL30 SEM-FEG) images were taken at the Shared Materials Instrumentation Facility at Duke University. Transmission electron microscopy–energy-dispersive X-ray spectroscopy (TEM–EDS) mapping (Super X EDS System) was performed at North Carolina State University. Copper TEM grids with a thin coating of carbon (400 mesh, SPI, #3540C-FA) were used to support

the nanowires. Once deposited on a grid, each sample was dried completely under a flow of nitrogen. Cyclic voltammetry (CV) experiments were performed with a model CHI601D electrochemical workstation (CH Instruments, Austin, TX) at room temperature. The three-electrode system consisted of a $\sim 0.5 \text{ cm} \times 2.5 \text{ cm}$ acetic acid treated piece of Cu foil as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl reference electrode (0.198 V vs. NHE). A 0.2 M Na_2SO_4 solution was used as the electrolyte. All potentials are reported versus Ag/AgCl unless otherwise stated. Metal concentration measurements were completed using a PerkinElmer 3100 atomic absorption spectrophotometer (AAS). For all NW films, transmittance and absorption data were collected using a UV–vis–NIR spectrophotometer (Cary 6000i), and sheet resistance values were measured using a four-point probe (Signatone SP4–50045TBS). The data points in Figure 5A and B are an average of five probe measurements.

3. RESULTS AND DISCUSSION

Figure 1, panels A–C summarize the process of fabricating Cu NW networks from solution without silver. The dispersed Cu NWs (Figure 1A) are transferred to a nitrocellulose based ink and deposited onto a glass substrate via a Meyer rod (Figure 1B) resulting in a randomly dispersed network of NWs that is not conductive. If 0.39 mM $AgNO_3$ is added to a stirring Cu NW storage solution with 0.58 M ascorbic acid and 1% PVP (to hinder nanowire aggregation), the NWs are evenly coated with silver. After this silver coating, the color of the NWs becomes more gray (Figure 1D). The Cu–Ag NWs can then be purified and made into transparent films in the same manner as Cu NWs (Figure 1E) but are conductive as printed with a sheet resistance of $31 \Omega \text{ sq}^{-1}$ at 79% T. This performance can be further improved to $29 \Omega \text{ sq}^{-1}$ at 84% T with a brief rinse in acetone and water to remove any remaining nitrocellulose and PVP (Figure 1F). No silver nanoparticles were observed either in the solution or in the films after coating, indicating that Ag was reduced only onto the surface of the NWs. The ease of fabrication and the minimal post processing necessary for films of Cu–Ag NWs is comparable to pure Ag NWs, for which a

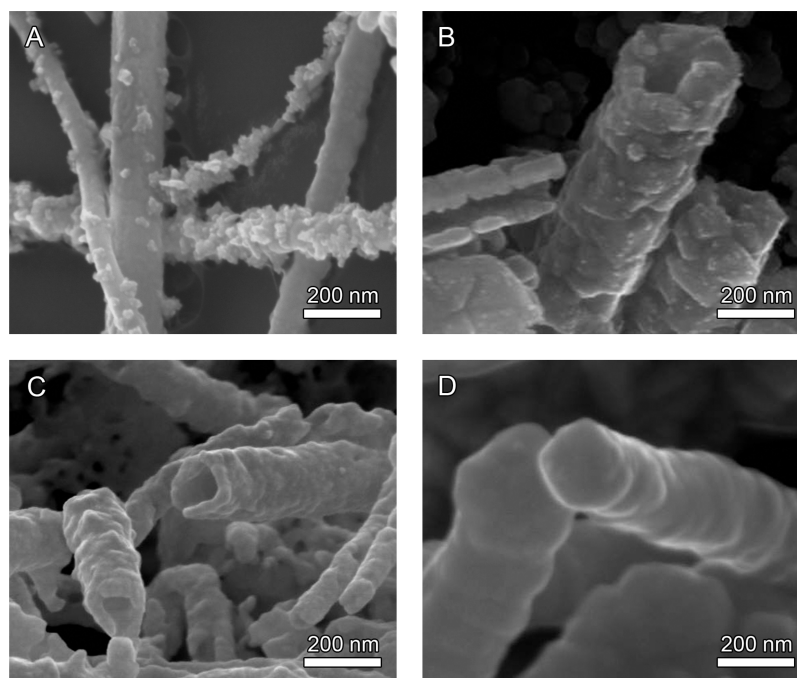


Figure 3. (A) SEM image of Cu–Ag NWs with 0 M ascorbic acid. SEM images of (B) Cu–Ag and (C) Cu–Au nanotubes made by immersing a Cu NW film in 0.025 M AgNO_3 or HAuCl_4 , respectively, after washing the Cu NWs with ascorbic acid. (D) SEM image of Cu–Ag NWs after a 0.58 M ascorbic acid wash and immersion into a solution with 0.58 M ascorbic acid and 0.025 M AgNO_3 .

mild heating step (at ≥ 120 °C) is usually required to remove any organics and anneal the NWs after coating.^{9,29}

Figure 2, panels A and B show SEM images of the Cu NWs before and after coating with silver. The diameter of the NWs increased by 13 nm after coating, and although the surface of the NWs appears to be slightly rougher, there are no indications that the NWs are galvanically etched by Ag^+ ions in the presence of ascorbic acid. Figure 2, panel C shows a SEM image of the Cu–Au NWs produced when AgNO_3 was replaced with HAuCl_4 , keeping all the other reaction conditions constant. Again, the average diameter of the NWs increased by 14 nm, and there is no evidence of etching. The TEM–EDS images in Figure 1, panels D and E further show that the NWs consist of a principally copper core with shells made of either silver or gold, respectively. Figure SI-1 shows that platinum can also be coated on the NWs with similar results.

If the synthesis of Cu–Ag NWs was attempted without ascorbic acid, the silver appeared to deposit as particles on the surface of the Cu NWs, and films of these NWs were not conductive (Figure 3A). It has previously been shown by Sun and Xia that a solution containing metal ions with a relatively high reduction potential (e.g., Au^{3+}) can galvanically etch nanostructures made from a less noble metal (e.g., Ag), resulting in a hollow version of the starting nanostructure.³⁰ However, the Cu NWs did not form hollow nanotubes in the absence of ascorbic acid. We hypothesized that copper oxide on the surface of the Cu NWs was hindering their reaction with silver. The silver particles forming on the surface of the Cu NWs might be due to some defects in this oxide coating.

To test if this hypothesis was correct, we first washed films of Cu NWs with ascorbic acid to remove the surface oxide. After the ascorbic acid wash, the Cu NW network became conductive, exhibiting a sheet resistance of $35 \Omega \text{ sq}^{-1}$ at 81% T. This change from a nonconductive to conductive state indicates the copper oxide layer on the NWs was dissolved by

the ascorbic acid in a similar manner as has been previously reported for acetic acid and lactic acid.^{13–15} Indeed, films of Cu NWs washed with acetic acid instead of ascorbic acid resulted in comparable optoelectronic properties of $30 \Omega \text{ sq}^{-1}$ at 79.6% T. After removal of the copper oxide layer, the film was then dipped into a solution containing only 0.025 M AgNO_3 in water. Figure 3, panel B shows that if the Cu NWs were exposed to Ag^+ ions after removal of copper oxide, they indeed form the expected nanotubes due to galvanic etching of the copper by Ag^+ .

After washing with ascorbic acid, the Cu NW film was reacted in a similar manner with 0.025 M HAuCl_4 and 0.005 M K_2PtCl_6 in water, again resulting in the expected nanotubes (Figures 3C and SI-4, respectively). If instead the Cu NW film was immersed in a solution containing 0.58 M ascorbic acid and 0.025 M AgNO_3 after washing with 0.58 M ascorbic acid, a rough shell of silver was deposited on the NWs, and there was no evidence of nanotube formation (Figure 3D). Thus, it appears ascorbic acid has two roles: (1) removal of copper oxide from the surface of Cu NWs and (2) providing a source of electrons to prevent galvanic etching of the Cu NWs.

To further investigate the role of ascorbic acid in preventing galvanic replacement, cyclic voltammograms were taken with Cu foil as the working electrode (to simulate a Cu NW network) in aqueous solutions with different concentrations of ascorbic acid. As shown in Figure 4, in the absence of ascorbic acid (black curve), scanning the electrode beyond about 0.1 V results in oxidation of the copper electrode. In the reverse scan, there is only one wave at approximately -0.25 V that we attribute to the reduction of copper oxides or copper ions. After addition of as little as 6 mM ascorbic acid (red curve), the oxidation and rereduction currents both decreased, indicating that ascorbic acid suppressed the oxidation of copper. In addition, there is a small shoulder at -0.35 V due to the reduction of one or more ascorbic acid oxidation products.

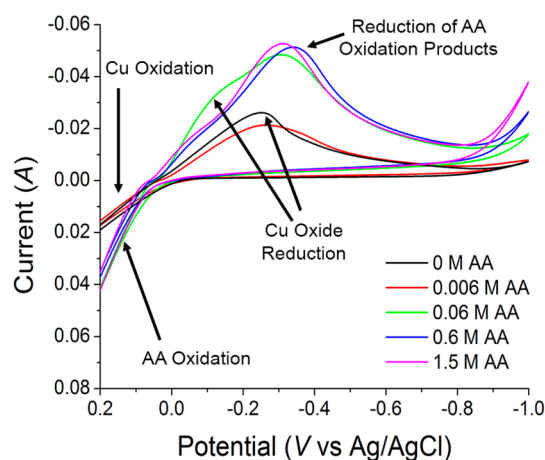


Figure 4. Cyclic voltammograms of copper foil in aqueous solutions of ascorbic acid (AA).

Further increasing the concentration of ascorbic acid results in oxidation of ascorbic acid instead of copper at positive potentials, resulting in more current. The reduction of the ascorbic acid oxidation product(s) at these higher concentrations in the reverse scan increases the cathodic peak at -0.35 V. At 0.06 M ascorbic acid (green line), there is a shoulder at -0.1 V that we attribute to the reduction of oxidized copper species, but this disappears at 0.6 and 1.5 M ascorbic acid, indicating that the oxidation of copper has been prevented completely. Thus, we see that, because of its greater potential to oxidize relative to Cu, sufficient amounts of ascorbic acid can completely prevent the oxidation of copper under oxidizing conditions.³¹

Finally we discuss the effect of the silver shell thickness on the optoelectronic properties and oxidation resistance of Cu–Ag NW films. Figure 5, panel A shows plots of transmittance (at a wavelength of 550 nm) versus sheet resistance for Cu–Ag NWs with various aspect ratios (L/D). The properties of Cu NWs with $L = 28.3$ μm and $D = 79$ nm ($L/D = 360$) and Ag NWs with similar dimensions ($L = 25$ μm , $D = 85$ nm, $L/D = 300$) are shown for comparison.²⁸ The Cu NWs, pure Ag NWs, and Cu–Ag NWs with $L/D = 320$ (~ 5 nm thick silver shell) all exhibit comparable performance and have similar transmittance spectra (see Figure SI-5). As the thickness of the silver shell is increased to 15 nm, the performance of the Cu–Ag NWs drops due to their lower aspect ratio ($L/D = 260$) and larger light scattering cross-section. The Cu–Au and Cu–Pt NW films exhibit higher sheet resistance values (see Figures SI-2 and SI-3) than Cu NWs, likely due to the relatively higher resistivity of gold ($\rho = 2.21 \times 10^{-8}$ Ω m) and platinum ($\rho = 10.5 \times 10^{-8}$ Ω m) compared to copper ($\rho = 1.7 \times 10^{-8}$ Ω m).

In contrast to the optoelectronic performance, the oxidation resistance of the Cu–Ag NWs generally improves with the thickness of the silver shell. The oxidation resistance of Cu–Ag NWs was measured by monitoring the sheet resistance of NW films as a function of time in dry and humid environments. In a dry oven at 160 $^{\circ}\text{C}$, the sheet resistance of the Cu NW films increased from 39 Ω sq^{-1} to 80 Ω sq^{-1} in only 30 min due to thermal oxidation (Figure 5B). The Cu–Ag NW samples of $L/D = 320$ and 260 remained conductive for at least 24 h, with sheet resistances increasing slightly from 26 to 49 Ω sq^{-1} and 25 to 33 Ω sq^{-1} , respectively. The oxidation resistance of the Cu–Ag NWs was thus similar to the stability of Ag NWs in the dry oven at 160 $^{\circ}\text{C}$.

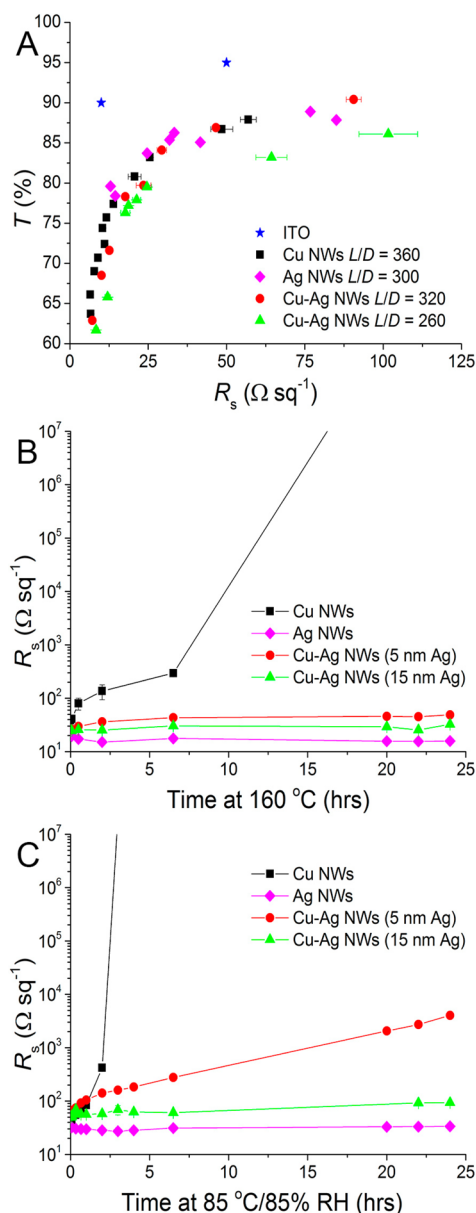


Figure 5. (A) Plots of transmittance versus sheet resistance for Cu NWs, Ag NWs, and Cu–Ag NWs with different aspect ratios (L/D). Plots of sheet resistance versus time for Cu NWs, Ag NWs, and Cu–Ag NWs in (B) a dry oven at 160 $^{\circ}\text{C}$ and (C) at 85 $^{\circ}\text{C}/85\%$ RH.

When subjected to a humid environment (85% RH) at 85 $^{\circ}\text{C}$, the sheet resistance of Cu NW films increases by orders of magnitude in a few hours (Figure 5C), but silver shells provided protection against oxidation. The sheet resistance of Cu–Ag NW films with an L/D of 320 (5 nm thick shell) exhibited an increase of about two orders of magnitude over 24 h and thus was not able to completely protect the copper core from oxidation under humid conditions. However, increasing the shell thickness to 15 nm ($L/D = 260$) enabled the Cu–Ag NW films to retain their sheet resistance over 24 h.

4. CONCLUSION

In summary, we show how to coat Cu NWs with shells of gold, silver, and platinum with a simple room-temperature, solution-phase process that does not galvanically etch and degrade the properties of the Cu NWs. In this process, ascorbic acid

dissolves the surface oxide off the Cu NWs and prevents oxidation of the Cu NWs while reducing the noble metal ions. Unlike Cu NWs, Cu–Ag NWs are conductive as printed, requiring minimal postprocessing to achieve the same optoelectronic properties as Ag NWs with the same aspect ratio. In addition, Cu–Ag NWs exhibit similar resistance to oxidation as Ag NWs. Thus, a thin shell of silver on Cu NWs can allow them to be coated from solution to create a conductive film that is resistant to oxidation with no extra steps, just as is the case for Ag NWs. The development of Cu–Ag NWs thereby eliminates a major practical hurdle to the use of copper-based NWs for making low-cost transparent conducting films for solar cells and OLEDs. In addition, we expect the ability to coat thin shells of valuable noble metals on an abundant base metal such as copper will have applications in conducting composites and electrocatalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.chemmater.5b03709](https://doi.org/10.1021/acs.chemmater.5b03709).

SEM image of Cu–Pt core–shell NWs; camera images showing the transition from Cu to Cu–Au NWs; DFOM image showing a network of Cu–Au NWs; DFOM image showing a network of Cu–Pt NWs; image of Cu–Pt nanotubes; transmittance spectra of Cu-based NWs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Benjamin.wiley@duke.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Samsung GRO grant, NSF Grant No. ECCS-1344745, and an NSF CAREER award (DMR-1253534). I.E.S. was supported by the Kathleen Zielek Fellowship through the Duke Chemistry Department. Z.-F.C. thanks the National Natural Science Foundation of China (21405114, 21573160) for support. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University.

■ REFERENCES

- (1) Gordon, R. G. Criteria for Choosing Transparent Conductors. *MRS Bull.* **2000**, *25*, 52–57.
- (2) Ye, S.; Rathmell, A. R.; Chen, Z.; Stewart, I. E.; Wiley, B. J. Metal Nanowire Networks: The Next Generation of Transparent Conductors. *Adv. Mater.* **2014**, *26*, 6670–6687.
- (3) Hecht, D. S.; Hu, L. B.; Irvin, G. Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures. *Adv. Mater.* **2011**, *23*, 1482–1513.
- (4) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. Transparent, Conductive Carbon Nanotube Films. *Science* **2004**, *305*, 1273–1276.

- (5) Bae, S.; Kim, H.; Lee, Y.; Xu, X.; Park, J.-S.; Zheng, Y.; Balakrishnan, J.; Lei, T.; Kim, H. R.; Song, Y. I.; Kim, Y.-J.; Kim, K. S.; Ozyilmaz, B.; Ahn, J.-H.; Hong, B. H.; Iijima, S. Roll-to-roll production of 30-in. graphene films for transparent electrodes. *Nat. Nanotechnol.* **2010**, *5*, 574–578.

- (6) Lee, J. H.; Shin, D. W.; Makotchenko, V. G.; Nazarov, A. S.; Fedorov, V. E.; Kim, Y. H.; Choi, J.-Y.; Kim, J. M.; Yoo, J.-B. One-Step Exfoliation Synthesis of Easily Soluble Graphite and Transparent Conducting Graphene Sheets. *Adv. Mater.* **2009**, *21*, 4383–4387.

- (7) Elschner, A.; Lövenich, W. Solution-deposited PEDOT for transparent conductive applications. *MRS Bull.* **2011**, *36*, 794–798.

- (8) Kirchmeyer, S.; Reuter, K. Scientific Importance, Properties and Growing Applications of Poly(3,4-ethylenedioxythiophene). *J. Mater. Chem.* **2005**, *15*, 2077–2088.

- (9) Song, M.; You, D. S.; Lim, K.; Park, S.; Jung, S.; Kim, C. S.; Kim, D.-H.; Kim, D.-G.; Kim, J.-K.; Park, J.; Kang, Y.-C.; Heo, J.; Jin, S.-H.; Park, J. H.; Kang, J.-W. Highly Efficient and Bendable Organic Solar Cells with Solution-Processed Silver Nanowire Electrodes. *Adv. Funct. Mater.* **2013**, *23*, 4177–4184.

- (10) Ye, S.; Rathmell, A. R.; Stewart, I. E.; Ha, Y.-C.; Wilson, A. R.; Chen, Z.; Wiley, B. J. A Rapid Synthesis of High Aspect Ratio Copper Nanowires for High-Performance Transparent Conducting Films. *Chem. Commun.* **2014**, *50*, 2562–2564.

- (11) U.S. Geological Survey. *Mineral Commodity Summaries. Copper*; U.S. Department of the Interior: Washington, DC, 2014; p 48.

- (12) Rathmell, A. R.; Wiley, B. J. The Synthesis and Coating of Long, Thin Copper Nanowires to Make Flexible, Transparent Conducting Films on Plastic Substrates. *Adv. Mater.* **2011**, *23*, 4798–4803.

- (13) Stewart, I. E.; Rathmell, A. R.; Yan, L.; Ye, S.; Flowers, P. F.; You, W.; Wiley, B. J. Solution-Processed Copper-Nickel Nanowire Anodes for Organic Solar Cells. *Nanoscale* **2014**, *6*, 5980–5988.

- (14) Mayousse, C.; Celle, C.; Carella, A.; Simonato, J.-P. Synthesis and Purification of Long Copper Nanowires. Application to High Performance Flexible Transparent Electrodes with and without PEDOT:PSS. *Nano Res.* **2014**, *7*, 315–324.

- (15) Won, Y.; Kim, A.; Lee, D.; Yang, W.; Woo, K.; Jeong, S.; Moon, J. Annealing-Free Fabrication of Highly Oxidation-Resistive Copper Nanowire Composite Conductors for Photovoltaics. *NPG Asia Mater.* **2014**, *6*, e105.

- (16) Rathmell, A. R.; Nguyen, M.; Chi, M.; Wiley, B. J. Synthesis of Oxidation-Resistant Cupronickel Nanowires for Transparent Conducting Nanowire Networks. *Nano Lett.* **2012**, *12*, 3193–3199.

- (17) Chen, Z.; Ye, S.; Stewart, I. E.; Wiley, B. J. Copper Nanowire Networks with Transparent Oxide Shells That Prevent Oxidation without Reducing Transmittance. *ACS Nano* **2014**, *8*, 9673–9679.

- (18) Kholmanov, I. N.; Domingues, S. H.; Chou, H.; Wang, X.; Tan, C.; Kim, J.-Y.; Li, H.; Piner, R.; Zabin, A. J. G.; Ruoff, R. S. Reduced Graphene Oxide/Copper Nanowire Hybrid Films as High-Performance Transparent Electrodes. *ACS Nano* **2013**, *7*, 1811–1816.

- (19) Hsu, P. C.; Wu, H.; Carney, T. J.; McDowell, M. T.; Yang, Y.; Garnett, E. C.; Li, M.; Hu, L.; Cui, Y. Passivation Coating on Electrospun Copper Nanofibers for Stable Transparent Electrodes. *ACS Nano* **2012**, *6*, 5150–5156.

- (20) Im, H.-G.; Jung, S.-H.; Jin, J.; Lee, D.; Lee, J.; Lee, D.; Lee, J.-Y.; Kim, I.-D.; Bae, B.-S. Flexible Transparent Conducting Hybrid Film Using a Surface-Embedded Copper Nanowire Network: A Highly Oxidation-Resistant Copper Nanowire Electrode for Flexible Optoelectronics. *ACS Nano* **2014**, *8*, 10973–10979.

- (21) Kim, T.; Canlier, A.; Cho, C.; Rozyyev, V.; Lee, J.-Y.; Han, S. M. Highly Transparent Au-Coated Ag Nanowire Transparent Electrode with Reduction in Haze. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13527–13534.

- (22) Yang, Y.; Liu, J.; Fu, Z.-W.; Qin, D. J. Galvanic Replacement-Free Deposition of Au on Ag for Core–Shell Nanocubes with Enhanced Chemical Stability and SERS Activity. *J. Am. Chem. Soc.* **2014**, *136*, 8153–8156.

- (23) Tsai, C.-H.; Chen, S.-Y.; Song, J.-M.; Chen, I.-G.; Lee, H.-Y. Thermal stability of Cu@Ag core–shell nanoparticles. *Corros. Sci.* **2013**, *74*, 123–129.

(24) Chee, S.-S.; Lee, J.-H. Preparation and oxidation behavior of Ag-coated Cu nanoparticles less than 20 nm in size. *J. Mater. Chem. C* **2014**, *2*, 5372–5381.

(25) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, *25*, 6313.

(26) Anderson, B. D.; Tracy, J. B. Nanoparticle conversion chemistry: Kirkendall effect, galvanic exchange, and anion exchange. *Nanoscale* **2014**, *6*, 12195–12216.

(27) Wiley, B.; Sun, Y. G.; Xia, Y. N. Polyol Synthesis of Silver Nanostructures: Control of Product Morphology with Fe(II) or Fe(III) Species. *Langmuir* **2005**, *21*, 8077–8080.

(28) Bergin, S. M.; Chen, Y. H.; Rathmell, A. R.; Charbonneau, P.; Li, Z. Y.; Wiley, B. J. The Effect of Nanowire Length and Diameter on the Properties of Transparent, Conducting Nanowire Films. *Nanoscale* **2012**, *4*, 1996–2004.

(29) Hu, L. B.; Kim, H. S.; Lee, J. Y.; Peumans, P.; Cui, Y. Scalable Coating and Properties of Transparent, Flexible, Silver Nanowire Electrodes. *ACS Nano* **2010**, *4*, 2955–2963.

(30) Sun, Y.; Xia, Y. Mechanistic Study on the Replacement Reaction between Silver Nanostructures and Chloroauric Acid in Aqueous Medium. *J. Am. Chem. Soc.* **2004**, *126*, 3892–3901.

(31) Xiong, J.; Wang, Y.; Xue, Q.; Wu, X. Synthesis of Highly Stable Dispersions of Nanosized Copper Particles Using L-Ascorbic Acid. *Green Chem.* **2011**, *13*, 900–904.