

Synthesis of Oxidation-Resistant Cupronickel Nanowires for Transparent Conducting Nanowire Networks

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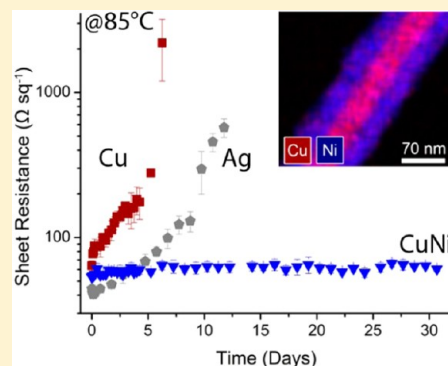
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S Supporting Information

ABSTRACT: Nanowires of copper can be coated from liquids to create flexible, transparent conducting films that can potentially replace the dominant transparent conductor, indium tin oxide, in displays, solar cells, organic light-emitting diodes, and electrochromic windows. One issue with these nanowire films is that copper is prone to oxidation. It was hypothesized that the resistance to oxidation could be improved by coating copper nanowires with nickel. This work demonstrates a method for synthesizing copper nanowires with nickel shells as well as the properties of cupronickel nanowires in transparent conducting films. Time- and temperature-dependent sheet resistance measurements indicate that the sheet resistance of copper and silver nanowire films will double after 3 and 36 months at room temperature, respectively. In contrast, the sheet resistance of cupronickel nanowires containing 20 mol % nickel will double in about 400 years. Coating copper nanowires to a ratio of 2:1 Cu:Ni gave them a neutral gray color, making them more suitable for use in displays and electrochromic windows. These properties, and the fact that copper and nickel are 1000 times more abundant than indium or silver, make cupronickel nanowires a promising alternative for the sustainable, efficient production of transparent conductors.

KEYWORDS: Nickel, copper, nanowires, transparent conductor



Flat-panel TVs, e-readers, smart-phones, smart-glass, touch-screens, organic light-emitting diodes, and organic solar cells all require a layer that allows for charge transport without blocking the transmission of light.^{1–11} ITO is used for most applications because of its high performance (transmittance on glass >90% at 10 Ω sq⁻¹), but indium is scarce, ITO is brittle and easily cracks, and ITO film is expensive.^{1,12} Much of the cost of ITO film results from a vapor-phase coating process that is 1000 times slower than liquid coating processes such as newspaper printing.¹²

The limitations of ITO have motivated a search for alternatives that are flexible, affordable, and can be deposited from liquids at high coating rates (>1 m s⁻¹). Conducting polymers such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) have good performance at high sheet resistances (>300 Ω sq⁻¹), but they cannot match the performance of ITO at lower sheet resistances (<100 Ω sq⁻¹).^{13,14} Solution-coated films of carbon nanotubes are another flexible alternative to ITO, but to date they have a relatively low performance due to the high junction resistance between nanotubes.^{13,15–28} Solution-coated films of silver nanowires have a transmittance and sheet resistance equivalent to ITO,^{29–36} but the price of silver (\$1000 kg⁻¹) is even greater than that of indium (\$800 kg⁻¹).³⁷

Copper ($\rho = 17$ nΩ m) is slightly less conductive than silver (16 nΩ m), but it is 1000 times more abundant and 100 times

less expensive (\$9 kg⁻¹).³⁸ Motivated by these intrinsic advantages of copper, we developed a scalable synthesis to produce long (>20 μm), thin (<60 nm), well-dispersed copper nanowires.³⁹ We demonstrated the scalable coating of a copper nanowire ink onto a plastic substrate to create flexible, transparent conducting films with a sheet resistance of 30 Ω sq⁻¹ at a transmittance of 85%.⁴⁰ These values make films of copper nanowires among the highest-performing solution-coatable alternatives to ITO. However, two problems hinder the practical implementation of copper nanowire films: (1) copper oxidizes, and (2) copper is reddish-orange in color, an undesirable characteristic for displays.

Alloying copper with nickel makes it gray in color and highly resistant to oxidation. For these reasons, cupronickel is widely used in coinage (the U.S. nickel is a 3:1 Cu:Ni alloy), as well as salt-water marine applications (boat hulls, propellers, etc.). There is only one previous paper that describes the production of copper nanowires with a nickel coating in a “one-pot” synthesis.⁴¹ In this work, the nanowires were 200–300 nm in diameter, with the outer 20–30 nm consisting primarily of nickel. Although this work represents a good first step, the diameters of these nanowires are too large to be suitable for use

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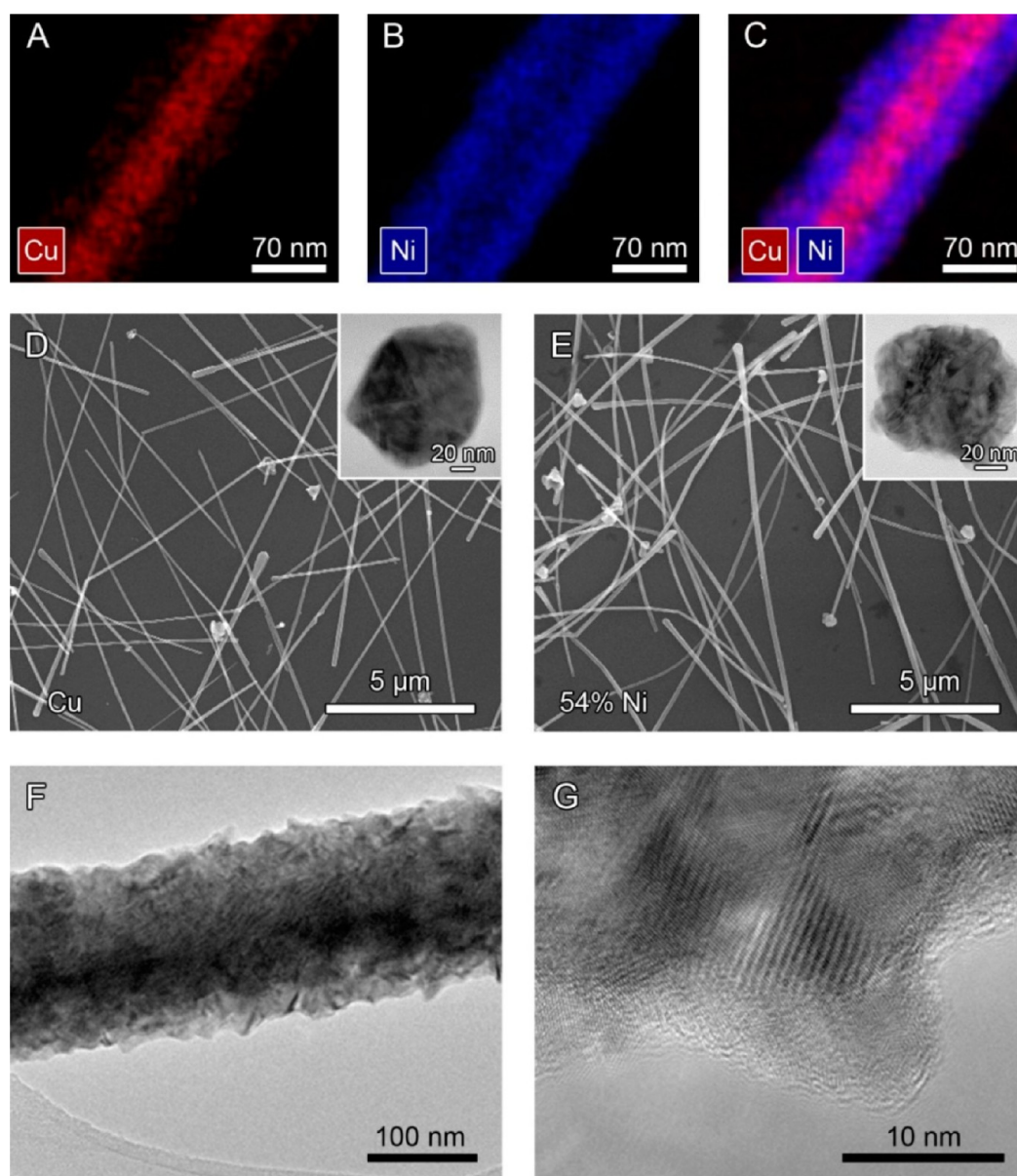


Figure 1. (A–C) Energy dispersive X-ray spectroscopy images of a copper nanowire coated with 54 mol % nickel. (D) Copper nanowires before coating. The nanowires had a length of $28.4 \pm 7.1 \mu\text{m}$ and a diameter of $75 \pm 19 \text{ nm}$. (E) After the copper nanowires were coated with nickel to a concentration of 54 mol %, the diameter of the wires increased to $116 \pm 28 \text{ nm}$. The insets of (D) and (E) show the cross sections of the copper nanowire and cupronickel nanowire, respectively. (F, G) TEM images of the polycrystalline cupronickel nanowires with a grain size of 10 nm.

in high-performance transparent conductive films, and the nanowires could be produced only at one copper-to-nickel ratio (13:7); other ratios produced spikey, spherical particles.

Here we report a new two-step approach to coating and alloying copper nanowires with nickel that allows for the production of thinner nanowires across a range of nickel concentrations. We further demonstrate the coating of cupronickel nanowires from a liquid carrier to create high-performance, transparent, conductive nanowire networks that are neutral gray in color and highly resistant to oxidation.

Copper nanowires, donated from NanoForge Corp., were synthesized in a manner similar to that which was reported previously.⁴⁰ The nanowires were stored at a copper nanowire concentration of 1.4 mg mL^{-1} in an aqueous solution containing polyvinylpyrrolidone (PVP, 1 wt %) and diethylhydroxylamine (1 wt %). Cupronickel nanowires were synthesized

by adding the copper nanowire stock solution (0.732 mL) to a 20 mL scintillation vial containing a solution (1.32 mL) of PVP (2 wt %) in ethylene glycol, a given amount of a solution containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 M) in water (157, 78.7, 39.3, or $15.7 \mu\text{L}$ for nanowires containing 54, 34, 20, and 10% Ni, respectively), and hydrazine ($132 \mu\text{L}$, 35 wt %). This mixture was vortexed for 15 s and heated at 120°C for 10 min without stirring. During the heating step, the copper nanowires aggregated and floated to the top of the solution. As the Ni reduced onto the copper nanowires, they became darker in color. After heating for 10 min, the solution was removed with a pipet, and the nanowires were dispersed in a solution containing PVP (1 wt %) and hydrazine (3 wt %).

Figures 1A–C show energy-dispersive X-ray spectroscopy images of a copper nanowire coated with nickel to a content of 54 mol % (roughly 1:1 Cu:Ni). As shown in panel A, Cu is

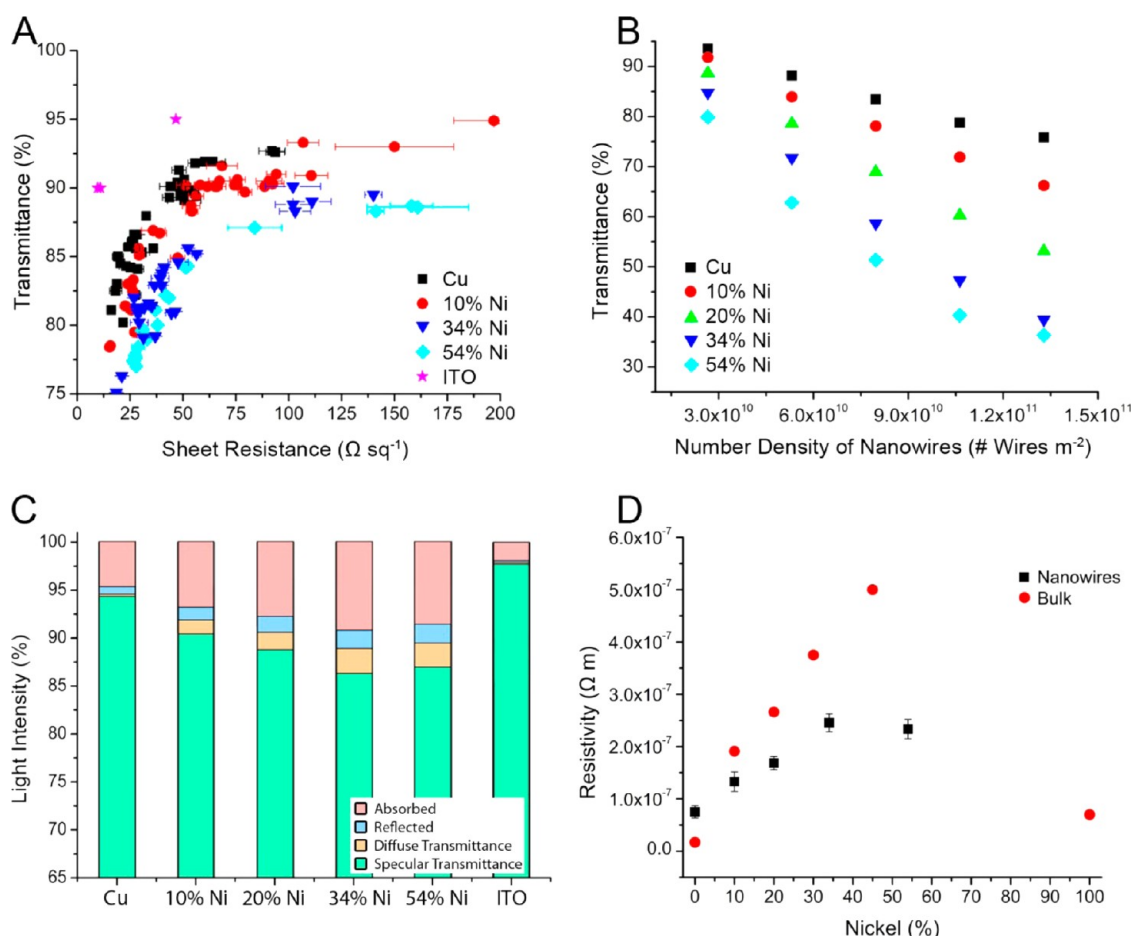


Figure 2. (A) Plot of specular transmittance ($\lambda = 550 \text{ nm}$) vs sheet resistance for films of copper nanowires, cupronickel nanowires, and ITO on glass (the light blocked by the glass was subtracted). Error bars show one standard deviation for five measurements. (B) A plot of specular transmittance vs number density of nanowires shows the effect of increasing wire diameter on the film's transmittance. (C) Graph comparing the absorbance, reflectance, diffuse transmittance, and specular transmittance ($\lambda = 550 \text{ nm}$) of ITO and nanowire films with different nickel contents. (D) Plot of resistivity vs nickel content for cupronickel nanowires and bulk cupronickel alloys. Error bars show one standard deviation for five measurements.

present not only in the core of the wire but also diffuses into the nickel shell, creating a shell composed of a cupronickel alloy. Since copper and nickel are completely miscible in all proportions, it is not surprising that these two elements interdiffuse after the nickel coating to form a nanowire consisting of a cupronickel alloy. Figure 1D shows the copper nanowires before coating; these nanowires had an average length of $28.4 \pm 7.1 \mu\text{m}$ and an average diameter of $75 \pm 19 \text{ nm}$. The inset is a TEM image of a microtomed cross section of a copper nanowire, showing that it has a 5-fold twinned crystal structure and a pentagonal cross section similar to silver nanowires synthesized in ethylene glycol.^{42,43} After coating to a wire composition of 54% Ni, the diameter of the nanowires increased to $116 \pm 28 \text{ nm}$ (Figure 1E). A TEM cross section of a microtomed cupronickel nanowire in the inset of Figure 1E shows the 5-fold twinned crystal structure became distorted and more randomly polycrystalline after alloying. It is not entirely clear why this transformation in the crystal structure took place, but this image seems to suggest that the diffusion of nickel into the copper nanowire caused a rearrangement of the copper atoms, and a conversion of the original 5-fold twinned crystal structure into one that is characterized by small, random crystal domains. TEM images (Figure 1F,G) of the 1:1 Cu:Ni

nanowires show that the nickel coating is polycrystalline with a grain size on the order of 10 nm.

To test their properties in the context of transparent conducting films, cupronickel nanowires were dispersed into a nitrocellulose-based ink and coated with a wire-wound metering rod (Meyer rod) onto glass slides in the same manner as was previously used for copper nanowires (see Supporting Information for details).⁴⁰ To remove organic material and anneal the cupronickel nanowire network, the films were plasma cleaned for 10 min in an atmosphere of 95% nitrogen and 5% hydrogen, followed by heating at 175°C under a flow of hydrogen in a tube furnace for 30 min. The transmittance and sheet resistance of the cupronickel nanowire network were measured using a UV/vis spectrophotometer and a four-point probe.

A plot of the specular transmittance (light with a horizontal beam divergence less than $\pm 3^\circ$ and a vertical beam divergence less than $\pm 7.5^\circ$) vs sheet resistance for ITO and copper nanowire networks alloyed with different amounts of nickel is shown in Figure 2A. This plot illustrates that the transmittance of the networks at a given sheet resistance decreases with increasing nickel content. For example, at a sheet resistance of $60 \Omega \text{ sq}^{-1}$, the transmittance drops from 94.4% to 84.3% ($\lambda = 550 \text{ nm}$) as the nickel content goes from zero to 54%. Part of

this decrease in transmittance is due to the fact that the diameter of the nanowires increased from 75 to 116 nm after they were coated with nickel to a concentration of 54%. Figure 2B illustrates that this increase in diameter resulted in a substantial decrease in the transmittance of a nanowire film with a given number density of nanowires. In Figure 2C, we see that this decrease in transmittance was due to a combination of increased absorption, scattering, and reflectance from the nanowires. For an increase in diameter from 75 to 116 nm, the amount of light that was absorbed increased from 4.7% to 8.6%, and the amount of light that was scattered or reflected from the nanowires increased from 1% to 4.5%.

Part of the decrease in performance can also be attributed to an increase in the resistivity of the nanowires. To measure the impact of nickel content on the resistivity of the nanowires, we filtered out the nanowires to make thick ($>0.5 \text{ g m}^{-2}$) films, in which the nanowires are all highly connected. The resistance of a thick nanowire film should be proportional to the mass of the nanowires. We then converted the mass of the nanowires in the film (m) to an effective thickness (t) by dividing it by the bulk density of the metal (ρ_B) and the area of the filter (A), as illustrated in eq 1.

$$t = \frac{m}{\rho_B A} \quad (1)$$

A plot of the resistance of the films versus the effective thickness gives a line with a slope equal to the resistivity of the nanowire network (Figure SI-1). Figure 2D shows the resistivity of the copper nanowire network ($\rho = 75.1 \text{ n}\Omega \text{ m}$) is 4.4 times greater than the resistivity of bulk copper ($\rho = 16.9 \text{ n}\Omega \text{ m}$).⁴⁴ This increase in resistivity is perhaps due to increased resistance at the junctions between nanowires. For comparison, the resistivity of electrodeposited copper nanowires of the same diameter ($\sim 50 \text{ nm}$) is $\sim 30 \text{ n}\Omega \text{ m}$,⁴⁵ the resistivity of bulk nanotwinned copper is $17.5 \text{ n}\Omega \text{ m}$, and the resistivity of bulk nanocrystalline copper can range from 30 to $150 \text{ n}\Omega \text{ m}$ for grain sizes of $\sim 20 \text{ nm}$.⁴⁴ Thus, the resistivity of the nanowire network is comparable to nanocrystalline copper.

Coating the copper nanowires with nickel to a concentration of 54 mol % increased the resistivity to $234 \text{ n}\Omega \text{ m}$, 3.1 times higher than pure copper nanowires. Causes for the relatively greater resistivity of the cupronickel nanowires likely include the intrinsically higher resistivity of nickel ($\rho = 70 \text{ n}\Omega \text{ m}$),⁴⁴ alloying of copper with nickel, and the polycrystalline nature of the cupronickel nanowires (the resistivity of nanocrystalline nickel with a grain size of 11 nm is $200 \text{ n}\Omega \text{ m}$).⁴⁴ Somewhat surprisingly, the cupronickel nanowires have a lower resistivity than the corresponding bulk alloy across all proportions.⁴⁶ For example, the resistivity of a cupronickel alloy containing 52 mol % nickel is $500 \text{ n}\Omega \text{ m}$. The lower resistivity of the cupronickel nanowires relative to the bulk alloy is likely due to the fact that the nanowires consist of a copper-rich core and a nickel-rich shell rather than a homogeneous alloy.

Although the addition of nickel to the copper nanowires results in a lower transmittance at a given sheet resistance, it greatly improves their resistance to oxidation. To test the resistance of cupronickel nanowires to oxidation, we put films of comparable transmittance (85–87% T) in an oven heated to 85°C and periodically measured their sheet resistance over time. Figure 3A shows that, without any nickel coating, the sheet resistance of the copper nanowire film began to increase after 1 day and increased by an order of magnitude after 5 days. The sheet resistance of silver nanowire films increased by an

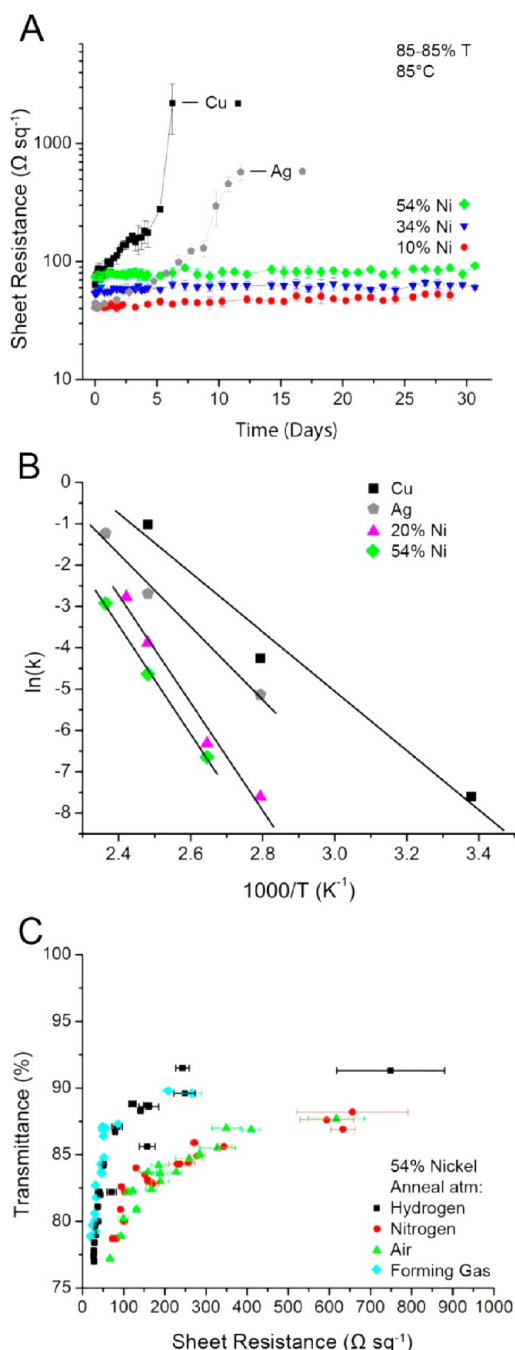


Figure 3. (A) Plot of sheet resistance vs time for films of silver nanowires, copper nanowires, and cupronickel nanowires stored at 85°C . (B) An Arrhenius plot of $\ln(k)$ vs $1000/T$ illustrates the temperature-dependent stability of the nanowire films. (C) Plot of transmittance vs sheet resistance for cupronickel nanowire films annealed in various atmospheres. All error bars show one standard deviation of five measurements.

order of magnitude after 13 days. In comparison, with as little as 10% nickel relative to copper (9:1 Cu:Ni), the sheet resistance of the cupronickel nanowire film remained remarkably stable over a period of 30 days, increasing by only $10 \Omega \text{ sq}^{-1}$ (from 30 to $40 \Omega \text{ sq}^{-1}$). With Ni contents of 34% or greater, the change in the sheet resistance over 30 days is so small as to be within the error of the measurement.

In order to provide an estimate of the stability of the nanowires at room temperature, we measured the normalized

increase in the sheet resistance ($\Delta R/R_0$) of the nanowire films vs time to extract a rate constant, k , at temperatures between 85 and 150 °C (see Figures SI-2 to SI-5). We restricted our analysis to temperatures less than 150 °C because at temperatures greater than 160 °C, a layer of Cu_2O can overgrow the NiO layer on cupronickel, and change the oxidation kinetics.⁴⁷ We also restricted our analysis to sheet resistance data for which $\Delta R/R_0 < 1$ because a doubling in the sheet resistance would be unacceptable for most applications. Furthermore, all the data for which $\Delta R/R_0 < 1$ could be best fit with a linear rate law, which greatly simplified the comparison between various nanowires and temperatures. Equation 2 gives the form of the linear rate law used in our analysis, in which t is time (h) and C is a constant. It was previously found that the oxidation of copper nanoparticles followed a similar linear rate law.⁴⁸

$$\Delta R/R_0 = kt + C \quad (2)$$

We plotted $\ln(k)$ versus $1000/T$ in Figure 3B to show that the oxidation of the nanowire films, like that of metal films and nanoparticles,^{48–50} can be described by an Arrhenius equation, given as eq 3.

$$\ln(k) = -E_a/R(1/T) + \ln(A) \quad (3)$$

Here E_a is the activation energy (J mol^{-1}), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T is the absolute temperature (K), and A is a frequency factor (h^{-1}). We determined the activation energy for the corrosion of nanowire films from the slopes of the lines in Figure 3B and summarized these in Table 1. The activation

Table 1. Arrhenius Plot Data for Cu, Ag, 4:1 Cu:Ni, and 1:1 Cu:Ni Nanowire Films

nanowire composition	E_a (kJ mol^{-1})	years to $\Delta R/R_0 = 1$ at 25 °C
Cu	60	0.2
Ag	73	3
4:1 Cu:Ni	108	400
1:1 Cu:Ni	109	1000

energy for the oxidation of the copper nanowires (60 kJ mol^{-1}) is close to values previously obtained for copper nanoparticles (69.2 kJ mol^{-1} for $T < 200$ °C and 54.3 kJ mol^{-1} for $T > 200$ °C).⁴⁸

The Arrhenius plot also allows us to estimate the time at which $\Delta R/R_0 = 1$ at room temperature (25 °C). These times, summarized in Table 1, are 0.2, 3, 400, and 1000 years for networks of copper, silver, 4:1 Cu:Ni, and 1:1 Cu:Ni nanowires, respectively. Although using an Arrhenius plot is a generally accepted way to correlate rates of oxidation at high temperatures to those at lower temperatures,⁵⁰ it should be noted that these rates apply only for dry air and may change depending on the composition of the surrounding atmosphere or matrix. Furthermore, due to their slow rate of corrosion, we cannot be certain that the activation energy for corrosion of silver and cupronickel at room temperature is consistent with the values listed in Table 1. That being said, it seems likely that the activation energy for the corrosion of these metals does not vary significantly from 25 to 85 °C, and thus we can reasonably conclude that the cupronickel nanowires are about 100 times more stable than silver nanowires.

Because of their sensitivity to oxidation, copper nanowires must be annealed under a pure hydrogen atmosphere in order to reduce copper oxides and allow the nanowires to fuse at their

junctions. The use of a pure hydrogen atmosphere is generally not desirable in a manufacturing environment as it introduces additional cost and safety concerns. The greater oxidation resistance of the cupronickel nanowires allows them to be annealed under a forming gas atmosphere (5% hydrogen, 95% nitrogen), which, unlike pure hydrogen, is not explosive. Figure 3B shows cupronickel nanowire films have similar performance when annealed under hydrogen or forming gas. The cupronickel nanowire films can even be annealed under nitrogen or air and achieve fairly good performance, although not quite as good as if hydrogen is present as a reducing agent in the annealing atmosphere.

In addition to the issue of oxidation, alloying copper with nickel can address the issue of color. The reddish-orange color of copper nanowires is an aesthetically undesirable feature that must be addressed if they are to be used in displays. Figures 4A and 4B show camera images of nanowire films ($\%T = 87\%$) on a black background and on a white backlight to simulate how they might appear in a display. The nanowire films change from a reddish color to a gray color around a nickel content of 20–30%. Figure 4C presents a quantitative comparison of color on a Hunter color scale. On this scale, +a corresponds to red, –a corresponds to green, +b corresponds to yellow, and –b corresponds to blue. Surprisingly, when presented on this scale, copper appears more neutral in color than ITO, which is yellow-green in color. This can be understood by noting that the optical spectra of nanowire films are generally more flat than films of ITO, and the peak transmittance of ITO lies close to the yellow-green region of the visible spectrum (Figure 4D). The graph in Figure 4C shows that the reddish-orange color of copper gradually disappears with increasing nickel content, and the color neutrality is roughly equivalent to that of silver at a nickel concentration of 34%.

Our previous studies have shown that, unlike ITO, copper nanowire films can retain their low sheet resistance after severe mechanical deformation.⁴⁰ To confirm that this flexibility is retained after coating the copper nanowires with nickel, films of 20% and 54% nickel were repeatedly bent from a radius of curvature of 10 mm to a radius of curvature of 2.5 mm. Figure SI-6 shows that the cupronickel films exhibited a small increase in sheet resistance after 1000 bends; the sheet resistance increased from 92 to $128 \Omega \text{ sq}^{-1}$ for the 20% Ni nanowires and 77 to $137 \Omega \text{ sq}^{-1}$ for the 54% Ni nanowires. In comparison, the sheet resistance of the ITO film increased from 43 to $16200 \Omega \text{ sq}^{-1}$ after 250 bends.

We have synthesized cupronickel nanowires in a range of compositions to examine the effect of nickel content on the transmittance, electrical resistance, oxidation kinetics, and color of cupronickel nanowire films. Although coating copper nanowires with nickel to a ratio of 1:1 Cu:Ni decreased the transmittance of the nanowire films from 94% to 84% at a sheet resistance of $60 \Omega \text{ sq}^{-1}$, it made the nanowire films 1000 times more resistant to oxidation than films of copper nanowires and 100 times more resistant to oxidation than films of silver nanowires. Coating the copper nanowires with nickel to a Cu:Ni ratio of 2:1 also gave them a neutral gray color comparable to silver. The excellent electro-optical performance, neutral color, and extreme oxidation resistance of cupronickel nanowires, combined with the fact that Cu and Ni are 1000 times more abundant than Ag, make cupronickel nanowires an attractive alternative to silver nanowires for the creation of transparent conducting films in printable, flexible electronic devices.

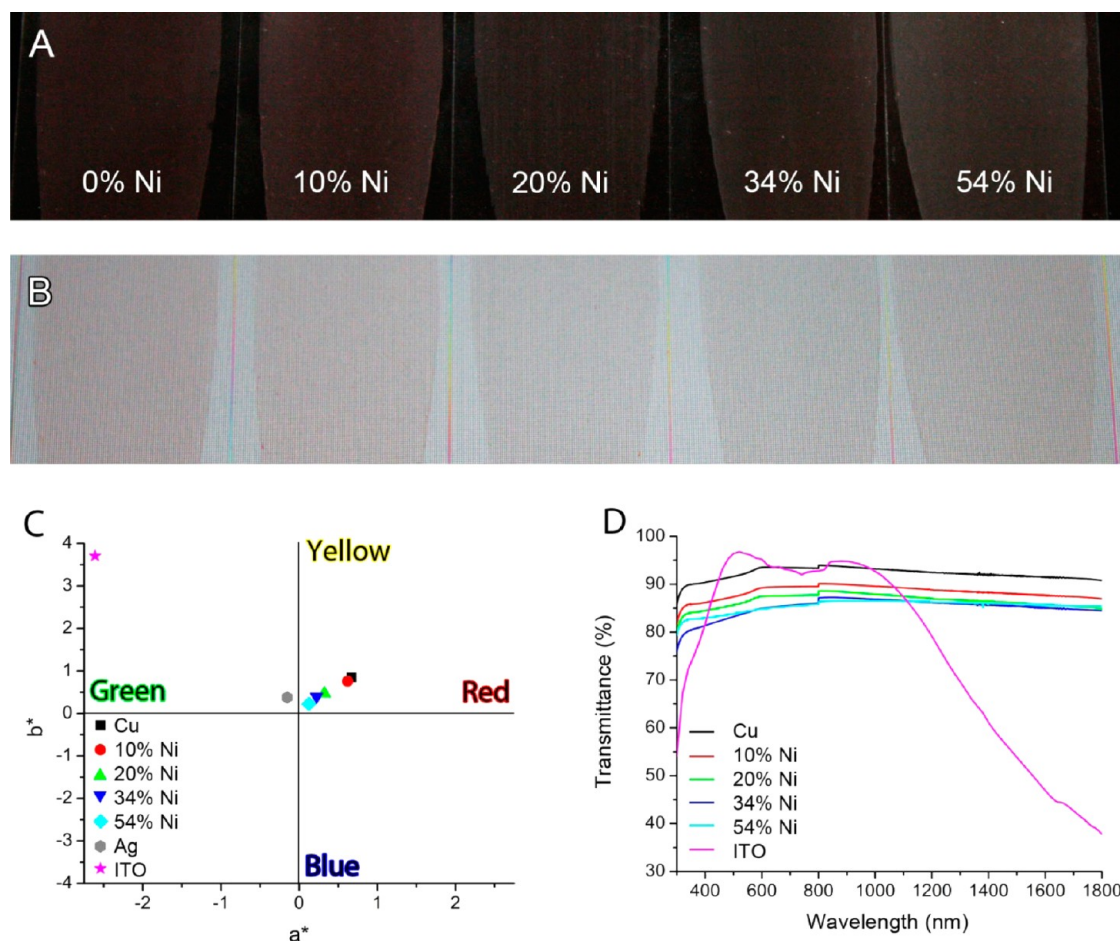


Figure 4. (A, B) Camera images of nanowire films ($\%T = 87\%$) on a black background and a white backlit display show the nanowire films change from a reddish-orange to gray color with increasing amounts of nickel. (C) Plot showing a quantitative comparison of color on a Hunter color scale. (D) Plot of transmittance vs wavelength for ITO ($11 \Omega \text{ sq}^{-1}$), copper nanowires, and cupronickel nanowires with different nickel contents. The nanowire films all have a sheet resistance of $60 \Omega \text{ sq}^{-1}$.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental materials, methods, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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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.

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