

The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films

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This communication shows that copper nanowires grow from spherical copper seeds in an aqueous solution of NaOH, ethylenediamine, $\text{Cu}(\text{NO}_3)_2$ and hydrazine. The longest ($10 \pm 3 \mu\text{m}$) and thinnest ($90 \pm 10 \text{ nm}$) nanowires were produced at an ethylenediamine concentration of 0.13 M; higher or lower concentrations led to the formation of shorter wires with larger diameters. Films of copper nanowires with a sheet resistance of $15 \Omega \text{ sq}^{-1}$ had a transmittance of 65%. Films of copper nanowires remained conductive and had no change in transmittance after storage in air for one month, and exhibited no change in sheet resistance after 1000 bending cycles. Calculated and experimental spectra suggest that the transmittance of conductive copper nanowire films can be increased to over 80% by reducing the aggregation of the nanowires.

The development of a high-performance transparent conductor that is also inexpensive, flexible, and can be deposited at low temperatures would remove a significant barrier to the development of low-cost flexible displays, lighting, and solar cells. Here we report the gram-scale synthesis of copper nanowires in aqueous solution, and their assembly into flexible films that transmit ~15% more light than films of carbon nanotubes with the same sheet resistance ($15\text{--}20 \Omega \text{ sq}^{-1}$). We further show that copper nanowires exhibit a unique growth mechanism in that they sprout and grow from spherical copper seeds.

Transparent conductors are used in a wide variety of applications, including low-emissivity windows, flat-panel displays, touch-sensitive control panels, and thin-film solar cells.^[1] The market for flat-panel displays alone is worth approximately \$90 billion per year.^[2] Display makers prefer to use Indium Tin Oxide (ITO) as the transparent conductor because it can be applied at relatively low temperatures compared to other conducting oxides, and is easier to etch than materials with comparable conductivities and transmittances.^[1] ITO films with a sheet resistance of $10 \Omega \text{ sq}^{-1}$ transmit about 90% of visible light.^[3] Limitations of ITO include the fact that it is brittle, and thus it cannot be used in flexible displays. The sputtering

process used to make ITO films is highly inefficient, depositing only 30% of an ITO target onto a substrate.^[4] Indium is also a scarce element, present in the earth's crust at concentrations of only 0.05 parts per million.^[5] The limited supply and increasing demand of indium for use in flat-panel displays, which represent 80% of indium consumption, has led to a recent price increase of 745%, from $\$94 \text{ kg}^{-1}$ in 2002, to about $\$700 \text{ kg}^{-1}$ today.^[4]

The brittleness, inefficient processing, and high cost of ITO films have motivated a search for alternatives. Films of carbon nanotubes (CNTs) have been extensively explored as one possible alternative, but nanotube films have yet to match the properties of ITO.^[6,7] More recently, researchers have shown flexible films of silver nanowires (AgNWs) have conductivities and transmittances comparable to ITO,^[8,9] but silver is also similar to ITO in price ($\$500 \text{ kg}^{-1}$) and scarcity (0.05 ppm).^[10]

Copper is 1000 times more abundant than indium or silver, and is 100 times less expensive.^[11] Films of copper nanowires (CuNWs) coated from water could thus represent a low-cost alternative to AgNWs or ITO for use as a transparent electrode.^[12] Here we show that CuNWs can be synthesized on the gram scale, filtered from solution, and printed onto a substrate to make transparent, conductive electrodes that perform substantially better than the best CNT electrodes. Our calculated and experimental spectra of nanowire films suggest that with further improvements in processing, the transmittance of CuNW films will exceed 80%. We also observe that CuNWs grow from spherical copper seeds in a way that is unique among all previously observed solution-based nanowire growth mechanisms.

We synthesized CuNWs by reducing $\text{Cu}(\text{NO}_3)_2$ with hydrazine in an aqueous solution containing NaOH and ethylenediamine (EDA), following the approach developed by Zeng and coworkers.^[13] Compared to this previous work, we have scaled up the reaction by 200 times (from 0.006 to 1.2 g of CuNWs) to demonstrate its potential for large-scale production. For the scale up reaction (Figure 1) NaOH (2000 mL, 15M), $\text{Cu}(\text{NO}_3)_2$ (100 mL, 0.2M), EDA (30 mL), and hydrazine (2.5 mL, 35 wt%) were added to a reaction flask and heated at 80°C for 60 minutes. The solution went from a royal blue (Figure 1a), indicative of Cu^{2+} ions, to a reddish brown color indicative of CuNW formation (Figure 1b) after 20 minutes. After the reaction, the CuNWs were washed with a 3 wt% aqueous solution of hydrazine, and stored in the same hydrazine solution at room temperature under an argon atmosphere to minimize oxidation.^[13]

Figure 1c shows a scanning electron microscope (SEM) image of the reaction product, consisting of CuNWs with a diameter of $90 \pm 10 \text{ nm}$, and a length of $10 \pm 3 \mu\text{m}$. An x-ray

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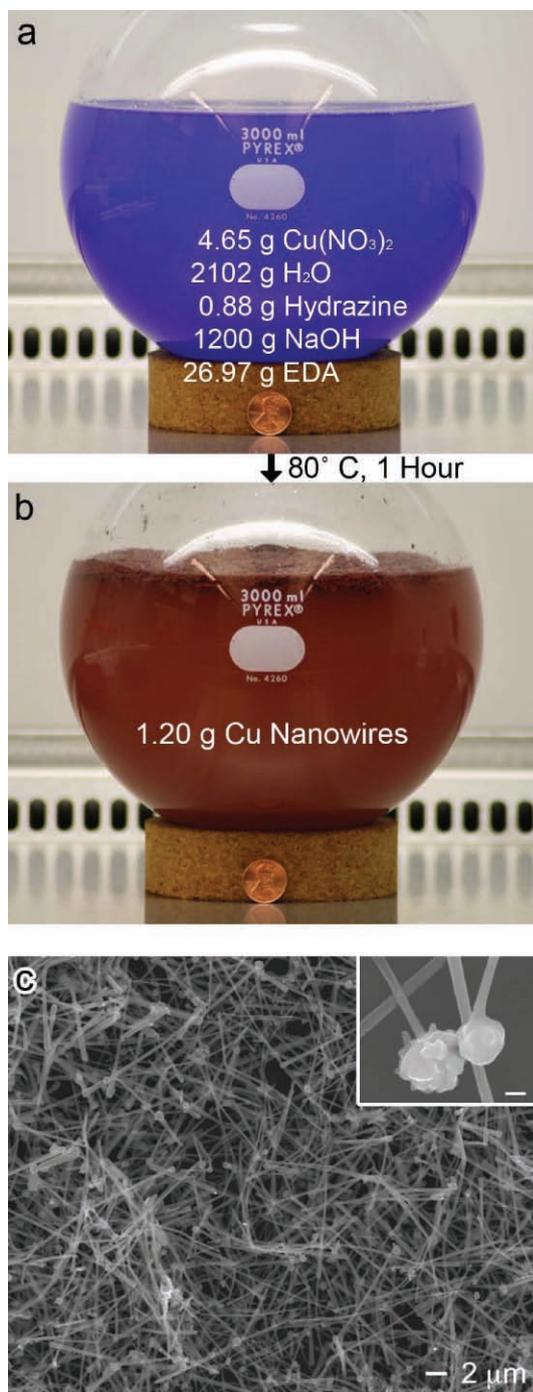


Figure 1. Pictures of the reaction flask (a) before the synthesis and (b) after growth of CuNWs at 80 °C for 1 hr. (c) SEM image of CuNW product. The nanowires are 90 ± 10 nm in diameter and 10 ± 3 μm in length. The inset shows CuNWs with a spherical copper particles attached at one end (scale bar = 200 nm).

diffraction pattern of this nanowire product confirms that the nanowires are FCC copper (Figure S1). The inset image shows a close up of the wires, in which it appears spherical nanoparticles are attached to one end of the nanowires. We could observe many similar wires with spherical nanoparticles attached at

one end, but initially it was not clear if the wires grew from the spherical nanoparticles, or if the spherical nanoparticles formed at the ends of the nanowires in the later stages of growth. These spherical particles at the ends of CuNWs have not previously been observed.

To determine if CuNWs did indeed grow from spherical seeds, we stopped the CuNW reaction at different times and examined the products with electron microscopy. These reactions were performed at a scale that was one hundred times smaller than that shown in Figure 1 with one-half the concentration of $\text{Cu}(\text{NO}_3)_2$ and EDA. As with the scale up reaction, the reaction color was initially blue, but became cloudy at 0.5 min., and clear at 2.5 min. The reaction mixture stayed clear until approximately 3 min. into the reaction, at which time we observed the first copper precipitate suspended in the solution. SEM images of this precipitate (Figure 2a) revealed CuNWs 100 ± 10 nm in diameter and less than 1 μm in length growing out of spherical nanoparticles. After reacting for 20 minutes (Figure 2b), wires grew to be 6 ± 1 μm in length, and were still attached to the spherical nanoparticles. The reaction was stopped after 60 minutes, at which time the CuNWs were 10 ± 3 μm in length, which was consistent with the length observed for the wires in the large-scale reaction. These images definitively show that CuNWs grew from spherical seeds. This growth mechanism has not been previously observed for CuNWs, and is further unique among all known solution-based syntheses of metal nanowires. The growth of Pt nanowires (PtNWs) from large, spherical aggregates of nanoparticles is somewhat similar in that both nanowires grow from spherical nanoparticles.^[14,15] The growth mechanisms differ in that hundreds of PtNWs grow from spherical aggregates in a structure similar to a sea urchin, where in the case of Cu, only one or two wires typically grow from a single seed.

To gain insight into the reason why CuNWs grew from spherical seeds, we examined the seed-nanowire interface with transmission electron microscopy (TEM). Figure 2c shows two CuNWs 70 nm in diameter that grew out of a spherical nanoparticle. The lack of any sharp difference in contrast between the nanoparticle and nanowire suggests the seed-wire interface consists of a single crystal. Figure 2d shows a selected area electron diffraction (SAED) pattern from the nanowire shown in Figure 2e. This pattern indicates the electron beam is oriented along the [110] zone axis, and that the nanowire grew along the $[1\bar{1}0]$ direction. We obtained the same SAED pattern from several nanowires, suggesting that the nanowires preferentially lay with a {110} facet in contact with the substrate. Unlike five-fold twinned AgNWs, there are no reflections from multiple zone axes.^[16] Thus, the SAED pattern further indicates that CuNWs consist of a single-crystalline domain, although the pattern does not rule out the presence of stacking faults on the {111} plane.^[17]

The CuNWs grew via atomic addition to {110} planes, which have the highest-surface energy among the low-index facets of copper and all other FCC metals.^[18–20] Single-crystalline nanostructures of Pb,^[19,22] Al,^[23] and Ag^[24] also grow via atomic addition to the {110} planes, but single-crystalline nanostructures of Au,^[25,26] Pt,^[13,14] and Rh^[27] grow via atomic addition to {111} planes. The lack of correlation between the surface

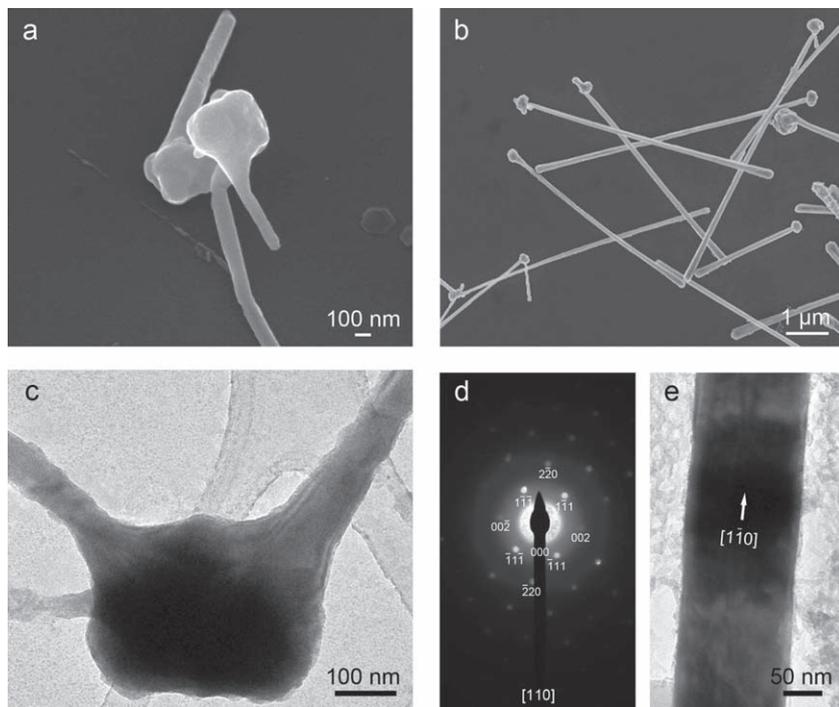


Figure 2. (a) SEM image showing copper nanorods sprouting from spherical copper seeds at a reaction time of 3.5 minutes. (b) By 20 minutes the rods had grown to form longer wires. (c) TEM image of two CuNWs growing out of a nanoparticle. (d) A selected area electron diffraction pattern (SAED) from the nanowire shown in (e) indicates the nanowire grew along the $[1\bar{1}1]$ direction.

energy of a metal and the direction of anisotropic growth in solution suggests that other forces besides surface energy drive anisotropic growth.

The addition of EDA to the reaction solution is necessary to promote anisotropic growth of CuNWs. When EDA was not added to the reaction, only spheres with diameters ranging from 125–500 nm were present after 1 hr. The amine groups of EDA allow it to bind to the surface of copper nanostructures in solution. If EDA binds preferentially to the side facets of the CuNWs, this could cause preferential growth along the axial $[110]$ direction. To examine the role of EDA as a possible director of anisotropic growth in the reaction, we studied the effect of EDA concentration on the diameter and length of the nanowires (Figure S2). As the concentration of EDA was increased from 0.04 M (the minimum necessary for formation of nanowires) to 0.13 M, the diameter of the nanowires decreased from 205 nm to 90 nm, while the length increased from 2 μm to 9 μm . Increasing the concentration of EDA further to 1.31 M increased the diameter by a factor of about three (260 nm) and decreased the length to 6 μm . This data suggests that low concentrations of EDA preferentially cap the sides of the wire, leading to anisotropic growth of long, thin nanowires. Higher concentrations of EDA may cause capping of wire ends as well as the sides, leading to shorter wires with larger diameters.

During the reaction, the CuNWs form a cake that floats on the top of the solution due to the bubbles of N_2 generated by decomposition of hydrazine. This aggregate of wires must be dispersed before the wires are used to make a transparent electrode.

To disperse the wires, they were sonicated in an aqueous solution containing 3 wt% of hydrazine and 1 wt% PVP. This solution was gently poured on top of 640 ml of a 10 wt% aqueous solution of PVP in a 1000 ml graduated cylinder. The Cu aggregates that were not dispersed during sonication settled to the bottom of the cylinder, leaving the well-dispersed NWs suspended in solution.

To examine their properties as transparent electrodes, the relatively well-dispersed CuNWs were filtered onto 0.6 μm polycarbonate membranes, and printed onto glass microscope slides coated with Aleene's Clear Gel Glue[®]. A thin film of glue was deposited onto the slides with a spin coater, and allowed to dry for one hour so that it hardened but remained sticky. The CuNW filtrate on the membrane was then put into contact with the sticky film by hand, and the membrane was peeled away, leaving the CuNWs on the clear glue. Figure 3a shows a camera image of a film containing 390 mg m^{-2} of CuNWs; this film has a transmittance of 67% ($\lambda = 500 \text{ nm}$) and a sheet resistance of 61 Ohm sq^{-1} .

The sheet resistance (R_s) and transmittance of the printed CuNW films were measured with a four-point probe (Signatone S-1160A-5) and a UV/VIS/NIR spectrometer (Cary 6000i), respectively. A plot of R_s versus nanowire

density shows there is an onset of percolation at a nanowire density of $\sim 350 \text{ mg m}^{-2}$ (Figure S3a), below which the films are not conductive. Figure S3b illustrates that the transmittance of the films decreases linearly with increasing nanowire density, indicating the transmittance is simply proportional to the open area that is not blocked by nanowires. Figure 3b shows plots of transmittance (at $\lambda = 500 \text{ nm}$) versus R_s for films of CuNWs 80 nm in diameter, along with other transparent conducting films for comparison. A film of CuNWs with a R_s of 15 Ohm sq^{-1} transmits $\sim 15\%$ more light than the best value reported for a film of CNTs with the same sheet resistance.^[28] The transmittance of the CuNW films is about 15% less than films of AgNWs,^[8] and 25% less than ITO.^[3]

To test the use of CuNW films as a flexible electrode, we subjected films with a transmittance of 60% to both compression and tensile bending, and measured the sheet resistance every 200 bend cycles. Each film started with a radius of curvature of 7.5 mm, and was bent until it reached a radius of curvature of 2.5 mm (Figure 3c).^[8] There was no change in sheet resistance after 1000 bending cycles.

As the stability of CuNWs is an area of concern for practical applications, we measured the sheet resistance of 818 mg m^{-2} films of CuNWs over 28 days. Figure 3d shows that films of CuNWs left in air at room temperature remain highly conductive for over one month. The surprising stability of these films in air suggests that proper packaging can easily ensure the long-term stability of CuNWs for practical applications.

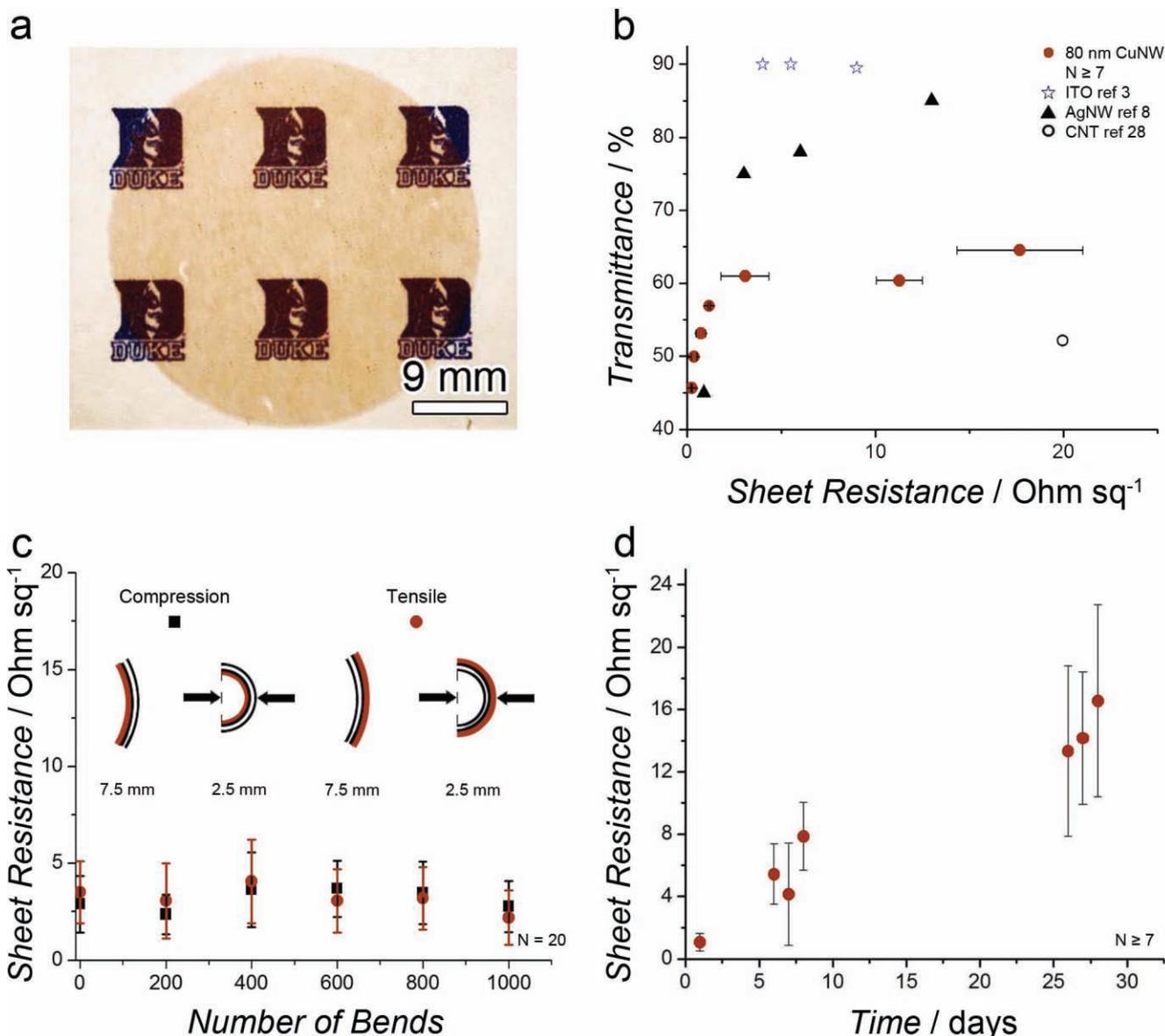


Figure 3. (a) Camera image of a CuNW film (390 mg m^{-2}) with a sheet resistance of $61 \text{ } \Omega \text{ sq}^{-1}$, and a transmittance of 67%. (b) Plot of transmittance versus sheet resistance for films of CuNWs (copper circles), silver nanowires (black triangles), ITO (blue stars), and carbon nanotubes (black open circle). Error bars show one standard deviation of the CuNW film's sheet resistance for ≥ 7 measurements. (c) A plot of sheet resistance versus number of bends shows no change in CuNW conductivity after 1000 bends. (d) A plot of sheet resistance versus time in days demonstrates the stability of the CuNW films.

Given that copper and silver have similar resistivities ($1.67 \text{ n}\Omega \text{ m}$ versus $1.59 \text{ n}\Omega \text{ m}$), it was surprising that CuNW films did not perform as well as films of AgNWs. To determine if the difference in performance between films of Ag and CuNWs was due to the optical properties of copper, we performed a finite-difference time-domain calculation to determine the transmittance of a periodic array of cylindrical nanowires consisting of Ag or Cu. The nanowires in the calculation were 80 nm in diameter and spaced $1 \text{ } \mu\text{m}$ apart (Figure 4a inset). Figure 4a shows that the transmittance of a CuNW grating is comparable to a grating consisting of AgNWs. Experimental spectra

(Figure 4b) further show that films of CuNWs transmit more light than films containing the same density of AgNWs with the same diameter (80 nm), and similar length (10 vs. $25 \text{ } \mu\text{m}$). The reason for the higher transmittance of CuNW films in this case is that the CuNWs are relatively clumped together, leaving more open space than the well-dispersed film of AgNWs (Figure 4c&d). This clumping also prevented the CuNW film from being conductive. In comparison, the AgNW film exhibited a low sheet resistance of $5.4 \text{ } \Omega \text{ sq}^{-1}$. This difference in conductivity cannot be accounted for by the difference in nanowire lengths alone. Well-dispersed films of AgNWs are conductive at lower

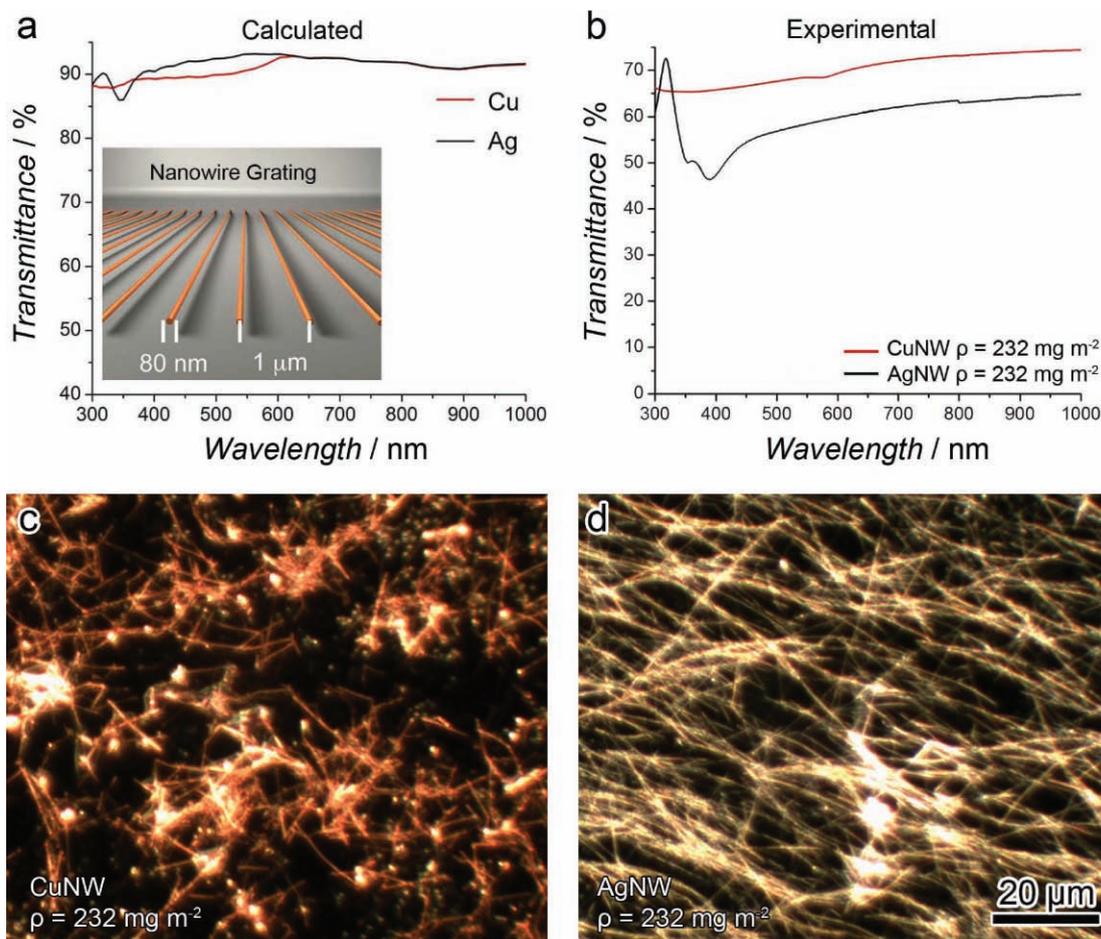


Figure 4. (a) Plot of the calculated transmittance (%) versus wavelength (nm) for copper (red) and silver (black) gratings consisting of cylindrical 80-nm wires spaced 1 μm apart. (b) Plot of experimental transmittance (%) versus wavelength (nm) for films of CuNWs (red) and AgNWs (black), both 80 nm in diameter and with the same density (232 g m⁻²). (c&d) Optical images showing the difference in (c) CuNW dispersion (nonconductive with a transmittance of 68%) and (d) AgNW dispersion ($R_s = 5.4 \text{ Ohms sq}^{-1}$ and a transmittance of 56%) for the same density of wires (232 mg m⁻²).

densities (higher transmittances) than CuNWs, not due to any large difference in the optical properties of the nanowires, but due to the fact that the AgNWs are more finely dispersed. We are currently developing synthetic methods that improve the dispersion of the CuNWs.

We have shown that CuNWs sprout and grow from spherical seeds, with the concentration of EDA being a critical parameter for their anisotropic growth. Films of CuNWs transmit ~15% more light than films of CNTs, but 25% less than ITO films with the same sheet resistance. Our calculations and experimental data indicate that the transmittance of CuNW films is not limited by the optical properties of copper, but by aggregation. If aggregation of CuNWs can be eliminated, the properties of films of CuNWs should be on par with films of AgNWs, and very close to those of ITO. With their low cost (copper is 1/100th the cost of indium), flexibility, and the fact they are grown in and deposited from aqueous solution, CuNWs could revolutionize the development and production of low-cost flexible displays,^[29] light emitting diodes,^[30] and thin film solar cells.^[1]

Experimental Section

See Supporting Information.

Supporting Information

Supporting Information is available online from Wiley InterScience or from the author.

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