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The Synthesis and Coating of Long, Thin Copper Nanowires to Make Flexible, Transparent Conducting Films on Plastic Substrates

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COMMUNICATION

This Communication describes the synthesis of long (>20 μ m), thin (<60 nm), well-dispersed copper nanowires and their scalable coating onto a plastic substrate to create flexible, transparent conducting films with a sheet resistance of 30 Ω sq⁻¹ at a transmittance of 85%. The motivation for this work was to create a flexible, high-performance transparent conducting film that could be coated at high rates from a liquid carrier, and thus enable lower production costs. Such low-cost transparent conducting films can potentially be used in a wide array of diverse applications, including thin-film solar cells, displays, and organic light-emitting diodes (LEDs).^[1] The copper nanowire films described here could carry high currents (>500 mA cm⁻²), were stable in air for over one month, and could be bent 1000 times without any degradation in their properties.

Indium tin oxide (ITO) is the transparent conductor of choice for most applications because of its high transmittance and conductivity, but it is scarce, brittle, and expensive.^[1a,2] The cost of ITO films is due not only to the fact that indium is a rare and costly material, but also because ITO must be deposited in an inefficient, low-throughput, vapor-phase coating process that, at 0.01 m s⁻¹, is 1000 times slower than wet-coating processes such as newspaper printing.

The limitations of ITO and other transparent conducting oxides have motivated a worldwide search for flexible, low-cost alternatives that can be deposited from liquids at coating rates orders of magnitude greater than vapor-phase coating processes. Solution-coated films of carbon nanotubes (CNTs) are one flexible alternative to ITO, but to date they have a relatively low transmittance and sheet resistance due to their absorbance of light and the poor electrical contact between nanotubes.^[3] The performances of solution-coated films of graphene are generally inferior to that of CNT films.^[4] Solution-coated films of silver nanowires (AgNWs) have a transmittance and sheet resistance close to ITO, but silver is also scarce and expensive.^[5]

Copper (resistivity $\rho = 1.59$ n Ω m) is nearly as conductive as silver (1.67 n Ω m), but it is 100 times less expensive and 1000 times more abundant.^[6] Motivated by these fundamental advantages of copper, we have recently reported a scalable synthesis of copper nanowires (CuNWs) and filtered them from solution to make transparent conducting films.^[7] However, the

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properties of the films were not as good as those made with AgNWs; at a sheet resistance of 15 Ω sq^-1, the transmittance of a AgNW film was about 85%, while that of a CuNW film was only 65%. Three reasons why the CuNW films were not as conductive as the AgNW films were the relatively short lengths (10 \pm 3 μ m), large diameters (90 \pm 10 nm), and aggregation of the nanowires.

Here we report a new synthesis that produces longer, thinner, well-dispersed CuNWs. These CuNWs were incorporated into an ink that could be coated onto a clear, plastic substrate to give a flexible, transparent conducting film with properties equivalent to films of AgNWs. In contrast to ITO, these films can withstand severe mechanical deformation and remain highly conductive.

To grow nanowires in our previous study, we kept the reaction mixture at a constant temperature (80 °C) throughout the nucleation and growth of the CuNWs.^[7] This resulted in the formation of nanowires that were relatively short (<10 μ m in length) and fat (>90 nm in width). Furthermore, the capping agent used in the synthesis, ethylenediamine (EDA), was found to be a poor dispersant for the CuNWs. As a result, aggregation of the CuNWs made it difficult to fabricate uniform films with high optical transmittance and low electrical resistance.

In an effort to improve the properties of transparent conducting films made from CuNWs, we developed a new synthesis to produce longer, thinner CuNWs that are also well dispersed. In order to grow longer, thinner wires, we heated the reaction mixture only a short time (about 3 min at 80 °C) in order to induce reduction of copper ions (as indicated from a change in the reaction color from blue to clear). Polyvinylpyrrolidone (PVP) was then added to this mixture to prevent the CuNWs from aggregating and this mixture was quickly cooled in an ice bath. This process allowed the CuNWs to grow at a lower temperature, resulting in a longer, thinner morphology. Interestingly, if PVP was added to the reaction before heating, only copper nanoparticles formed. In contrast, the addition of PVP to the reaction after the 3 min heating stage did not prevent nanowires from forming, but instead prevented the CuNWs from forming aggregates that could not be dispersed.

Once well-dispersed CuNWs were obtained, we wanted to demonstrate a scalable coating method for fabrication of transparent electrodes with CuNWs. In previous work, we filtered CuNWs from solution onto a membrane and transferred them onto a glass slide coated with clear glue. Although this method enables the fabrication of films from precise amounts of relatively clean nanowires, it is not a practical method for fabricating transparent electrodes over large areas. Spray coating is a potentially scalable method for fabrication of electrodes from

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carbon nanotubes^[3g] and AgNWs,^[1g] but it was difficult to spray CuNWs without the formation of aggregates unless relatively low concentrations of nanowires and high concentrations of polymer were used. As a result, spray coating proved to be slow, and we were not able to obtain high-quality electrodes with this method.

Yi Cui and co-workers have recently demonstrated Meyer rod coating of AgNWs to be a promising, scalable method for fabrication of transparent electrodes.^[5d] In their work, AgNWs were coated directly from methanol without the need for an additional film-forming polymer. This allowed the fabrication of transparent electrodes without a subsequent heating step to remove the polymer. Although this approach proved successful with AgNWs, we found it was not possible to obtain a uniform coating of CuNWs from methanol or other solvents without the addition of a film-forming material.

Ethyl cellulose is a widely used film former, and ink formulations made with ethyl cellulose proved successful in enabling the uniform coating of CuNWs. However, these films were not conductive unless the ethyl cellulose was burned away, which required high temperatures (>350 °C). Most flexible substrates cannot withstand such temperatures, and the thin nanowires tend to melt at temperatures greater than 250 °C. Thus we turned to nitrocellulose, which in addition to being an excellent film former, has a low autoignition temperature, and burns at 175 $^{\circ}\mathrm{C}$ without leaving behind much carbonaceous residue.

To make the CuNW ink formulation, the nitrocellulose was first dissolved in acetone, which readily dissolves the polymer. Ethanol and isopropyl alcohol were added to dilute the solution of nitrocellulose in acetone and enable the dispersion of CuNWs, which otherwise would not disperse in acetone because of their PVP-coating (PVP is not soluble in acetone). Ethyl acetate and pentyl acetate were added to improve spreading and leveling of the ink on the plastic substrate, and toluene was added to reduce the evaporation rate. After dispersing the CuNWs into this ink formulation, it was pipetted onto a polyethylene terephthalate (PET) substrate (**Figure 1**A) and spread with a Meyer rod to form a thin, uniform film (Figure 1B).

After the ink dried in air for about 5 min, we placed the film in a plasma cleaner under a forming gas atmosphere (5% hydrogen, 95% nitrogen) to remove as much of the nitrocellulose, PVP, and other organics as possible (Figure SI-1, Supporting Information), while also avoiding oxidation of the CuNWs, which occurred if the films were plasma cleaned in air. After plasma cleaning, the films had a sheet resistance of about 20 k Ω sq⁻¹. To finish removing the nitrocellulose and anneal the wires, the films were placed in a tube furnace with a pure hydrogen atmosphere at 175 °C. Since nitrocellulose has a



Figure 1. A,B) CuNW ink before and after coating on PET with a Meyer rod. C) A bent CuNW film (25 Ω sq⁻¹ and 83% transparent) completing an electrical circuit with a battery pack and a LED. D) Plot of current versus voltage for 40 Ω sq⁻¹ CuNW films, demonstrating their maximum current carrying capacity. E) Current vs. time plot for films of CuNWs (40 Ω sq⁻¹) and ITO (42 Ω sq⁻¹) with an applied voltage of 1.5 V over 24 h demonstrates the relative stability of CuNW films over time. The inset of (E) shows a visual comparison of ITO (10 Ω sq⁻¹) and CuNW (75 Ω sq⁻¹) films, both 88% transparent, backlit by an iPhone display.

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low auto ignition temperature, the remaining nitrocellulose vaporized and left a highly conductive network of CuNWs on PET.

To the best of our knowledge, this is the first demonstration of a highly conductive, transparent electrode made from CuNWs on PET. The scalable fabrication of a transparent conducting film of CuNWs on PET is particularly significant because PET is the most widely used substrate for fabrication of flexible, transparent conductive films. These films can be found in a wide array of products, including the e-ink displays used in most brands of e-readers, as well as signature pads at the grocery store checkout. To illustrate that the CuNW films can carry enough current (without oxidizing) to power display elements and lighting, while at the same time be highly flexible, we bent a film of CuNWs (25 Ω sq⁻¹ and 83% transparent) and put it into a circuit with a battery pack and a LED. As can be seen in Figure 1C, the bent film can easily carry enough current to power the LED.

The ability to carry large currents is an attractive feature for applications of transparent conducting films in photovoltaics and lighting. To measure the maximum current carrying capacity of the CuNW film, we tested a square of film with a sheet resistance

of 40 Ω sq⁻¹ at different voltage ramps. Figure 1D shows that the maximum current that can be obtained is 0.533 A $\rm cm^{-2}$ at a voltage ramp of 1.57 V s⁻¹, compared to 0.866 A cm⁻² at a voltage ramp of 1.61 V s⁻¹ for ITO (Figure SI-2, Supporting Information). This maximum current decreased to 0.42 A cm⁻² when the voltage ramp was reduced to 0.089 V s^{-1} . The slower voltage ramp resulted in a lower maximum current, likely because there was more time for the wires to resistively heat and melt. This lower current is enough to power six LEDs (similar to that in Figure 1C) at their maximum current rating. To test how the current carrying capacity of the CuNW film degraded over time in comparison to ITO, a voltage of 1.5 V (resulting in a current density of about half the maximum) was applied across the CuNW and ITO films for 24 h. Both of the films in Figure 1E show a similar amount of decay over time but are still conductive after 24 h. The inset of Figure 1E shows camera images of CuNW (75 Ω sq⁻¹) and ITO (10 Ω sq⁻¹) films with a transmittance of 88% against an iPhone backlight for a visual comparison of the color of the films. As expected the CuNW film appears slightly red and the ITO film appears slightly blue.

Figures 2A–D show optical and scanning electron microscopy (SEM) images of CuNW films to illustrate the relationship between the density of nanowires on the substrate and the properties of the film. Lower densities of CuNWs (Figures 2A,C) resulted in a higher transmittance (90%) and a higher sheet resistance (186 Ω sq⁻¹). As the density of the nanowires is increased (Figures 2B,D), both the transmittance (85%) and sheet resistance decreased (30 Ω sq⁻¹). The optical and SEM



Figure 2. A,B) Dark field optical microscope images showing uniformly dispersed networks of CuNWs that are 90% and 85% transparent with sheet resistances of 186 and 30 Ω sq⁻¹, respectively. C,D) Corresponding SEM images of the CuNW films from (A,B) showing the average length (20 ± 5 μ m) and diameter (52 ± 17 nm) of the CuNWs.

images show the improved synthesis and coating process yielded films that were highly uniform (not aggregated), which, in contrast to our previous work, enabled the films to have a high transmittance and low sheet resistance. The relationship between the transmittance and amount of CuNWs used in the film is given in **Figure 3**A. To obtain conductive films of CuNWs with a sheet resistance of 30 Ω sq⁻¹ requires only 0.06 g m⁻² of CuNWs.

The relationship between transmittance and sheet resistance for CuNW films is plotted in Figure 3B. At a sheet resistance of 50 Ω sq⁻¹, CuNW films made from these long, thin nanowires outperformed similar films of AgNWs^[5c,d] and CNTs^[3m,5b] made by Meyer rod coating and spray coating, respectively. AgNW films made by filtering wires onto a membrane from solution^[5c] slightly outperformed films of CuNWs at low sheet resistances. Continuous sheets of graphene also have superior performance to CuNWs and, unlike ITO, are flexible.^[8] However, this graphene has three disadvantages relative to films of CuNWs: 1) graphene is grown at a high temperature (1000 °C) over 30 min; 2) graphene is grown on a copper foil (\approx 200 g m⁻²) that is subsequently etched away; and 3) continuous, 2D sheets of graphene must be transferred whole to a substrate for an electrode to have high performance. Thus, although graphene has performance advantages, the lower processing temperatures, lower copper consumption, and the ability to coat CuNWs from solution at high rates potentially gives CuNWs an advantage over graphene in terms of cost.

Figure 3C shows what percentage of the light that is directed at a CuNW film is transmitted specularly (in our case, the



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Figure 3. A) Plot of transmittance (550 nm) vs. density (g m⁻²) of CuNWs in a film. B) Plot of transmittance (at a wavelength of 550 nm) vs. sheet resistance for films of CuNWs, AgNWs, ITO, graphene, and CNTs. Error bars show one standard deviation for 5 measurements. C) Graph showing specular transmittance, diffuse transmittance, reflectance, and absorbance (at a wavelength of 550 nm) for films of copper nanowires on PET and ITO. D) Plot of transmittance versus wavelength for ITO ($42 \Omega \text{ sq}^{-1}$) and films of CuNWs with different nanowire densities. E) Plot of sheet resistance versus number of bends for CuNW films (85% transparent) and ITO on PET. Inset shows the radius of curvature before (10 mm) and after bending (2.5 mm). F) Plot of sheet resistance versus time for CuNW films (89, 86, and 82% transparent from top to bottom) exposed to air for 42 d. Error bars show one standard deviation for 10 measurements.



detector accepts light with a horizontal beam divergence less than $\pm 3^{\circ}$ and a vertical beam divergence less than $\pm 7.5^{\circ}$), transmitted diffusely (scattered at an angle greater than the specularly transmitted light, but less than 180°), reflected, and absorbed. The diffusive transmittance is between 1.5% and 4% of the total light directed at the CuNW film, while for ITO it is less than 0.5%. Although diffusive transmittance is undesirable for displays, it can increase light capture in thin-film solar cells.^[5b,9] The reflectance of light from CuNW films is relatively significant, between 2.5% and 4.75%, whereas the reflectance from ITO films is nearly nonexistent. The transmittance of the CuNW films might be significantly increased through the application of an appropriate antireflective coating. For example, at a sheet resistance of $\approx 180 \Omega$ sq⁻¹, since only 5% of the light directed at the CuNW film is absorbed, the total transmittance can potentially be increased to 95%.

The total transmittance of ITO on glass with a sheet resistance of 45 Ω sq⁻¹ is still 7% greater than a film of CuNWs on PET at a wavelength of 550 nm. However, ITO is only more transparent than CuNW films with a similar sheet resistance at wavelengths between 400 and 1100 nm (Figure 3D). The greater transparency of CuNW films becomes especially dramatic at wavelengths greater than 1200 nm. For example, at the telecommunications wavelength of 1550 nm, the CuNW film has a transmittance of 87%, while ITO has a transmittance of 54%. Besides being useful for applications in communications, the greater transmittance of CuNW films in the infrared could be used to improve the efficiency of infrared photovoltaics.^[10]

A major advantage of films of metal nanowires is that they are much more flexible than brittle films of ITO. To demonstrate the flexibility of the CuNW films, films with a specular transmittance of 85% were subjected to both compression and tension bending from a radius of curvature of 10 mm to a radius of curvature of 2.5 mm (Figure 3E inset). Figure 3E illustrates that the CuNW films exhibited little change (30 Ω sq⁻¹ to 40 Ω sq⁻¹) in sheet resistance after 1000 bends. In contrast, the sheet resistance of ITO films increased by 400 times after just 250 bends.

In many of the applications in which transparent conducting films of CuNWs would be used, such as flexible displays, organic photovoltaics, and organic LEDs, there is already barrier materials in place to protect the organic component from oxygen and moisture. As copper is generally less sensitive to oxygen and moisture than these active organic components, oxidation of the CuNWs will likely not be an issue in these applications. That being said, resistance to oxidation is an advantage during manufacturing processes, as well as in applications where the CuNWs might be subjected to more corrosive conditions. In order to examine the oxidation rate of these new flexible electrodes, we left a variety of electrodes with different conductivities out in air and periodically measured their sheet resistance. Figure 3F shows that over a period of 42 d, the conductivity of the CuNW films remained fairly constant. There was a slight increase from day 1 to day 2, but from day 2 onward the sheet resistance remained within one standard deviation. This initial increase and subsequent stability may be due to a passivating layer of Cu₂O that formed on the surface of the CuNWs.^[11] Although this is not a comprehensive test of the resistance of CuNWs to oxidation under a variety of conditions, Figure 3F



illustrates that, even after plasma cleaning and annealing in hydrogen to remove the insulating organic material from the surface of the nanowires, the new thinner nanowires are fairly resistant to oxidation in air.

We have modified the solution-phase synthesis of CuNWs to double their length (from 10 to >20 μ m) and decrease their diameter (from 90 nm to <60 nm). These longer, thinner CuNWs were formulated into an ink that could be coated onto flexible plastic substrates to make transparent, conductive films that are equivalent to films of AgNWs in their performance. In contrast to ITO, films of CuNWs could be flexed 1000 times without degrading their sheet resistance and were highly transparent in the near-infrared. As the CuNW films now meet the transmittance and conductivity specifications required for practical applications, we expect these nanowires to enable the production of lower cost flexible displays, organic LEDs, and thinfilm photovoltaics.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. Experimental details are included in the Supporting Information.

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