The Impact of Morphology and Composition on the Resistivity and Oxidation Resistance of Metal Nanostructure Films

by

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Jie Liu

Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University

2016
ABSTRACT
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Abstract

Printed electronics, including transparent conductors, currently rely on expensive materials to generate high conductivity devices. Conductive inks for thick film applications utilizing inkjet, aerosol, and screen printing technologies are often comprised of expensive and rare silver particles. Thin film applications such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs) predominantly employ indium tin oxide (ITO) as the transparent conductive layer which requires expensive and wasteful vapor deposition techniques. Thus an alternative to silver and ITO with similar performance in printed electronics warrants considerable attention. Copper nanomaterials, being orders of magnitude cheaper and more abundant than silver or indium, solution-coatable, and exhibiting a bulk conductivity only 6% less than silver, have emerged as a promising candidate for incorporation in printed electronics.

First, we examine the effect of nanomaterial shape on the conductivity of thick films. The inks used in such films often require annealing at elevated temperature in order to sinter the silver nanoparticles together and obtain low resistivities. We explore the change in morphology and resistivity that occurs upon heating thick films of silver nanowires (of two different lengths, Ag NWs), nanoparticles (Ag NPs), and microflakes (Ag MFs) deposited from water at temperatures between 70 and 400 °C. At the lowest temperatures, longer Ag NWs exhibited the lowest resistivity ($1.8 \times 10^{-5} \, \Omega \, \text{cm}$),
suggesting that the resistivity of thick films of silver nanostructures is dominated by the contact resistance between particles.

This result supported previous research showing that junction resistance between Ag NWs in thin film conductors also dominates optoelectronic performance. Since the goal is to replace silver with copper, we perform a similar analysis by using a pseudo-2D rod network modeling approach that has been modified to include lognormal distributions in length that more closely reflect experimental data collected from the nanowire transparent conductors. In our analysis, we find that Cu NW-based transparent conductors are capable of achieving comparable electrical performance to Ag NW transparent conductors with similar dimensions. We also synthesize high aspect ratio Cu NWs (as high as 5700 in an aqueous based synthesis taking less than 30 minutes) and show that this increase in aspect ratio can result in transparent conducting films with a transmittance \( >95\% \) at a sheet resistance \( <100 \, \Omega \, \text{sq}^{-1} \), optoelectronic properties similar to that for ITO.

Two of the major barriers preventing the further use of Cu NWs in printed electronics are the necessity to anneal the nanowires under \( \text{H}_2 \) at higher temperatures and copper’s susceptibility to oxidation. We solve the former issue by removing the insulating oxide along the Cu NWs with acetic acid and pressing the nanowires together to make \( \text{H}_2 \) annealing obsolete. Finally, several methods of preventing copper oxidation in the context of transparent conductors were successfully developed such as
electroplating zinc, tin, and indium and electrolessly plating benzotriazole (BTAH), nickel, silver, gold, and platinum. While all of the shells lessened or prevented oxidation both in dry and humid conditions, we found that a thin layer of silver confers identical optoelectronic properties to the Cu NWs as pure Ag NWs. These results are expected provide motivation to replace pure silver and ITO in printed electronics.
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1. Introduction

Printed electronics manufactured through inkjet, aerosol, and screen printing technologies offer a low cost alternative for electronic device manufacturing compared to traditional lithography, etching, vacuum, or electroless plating techniques that are expensive and time consuming. With the market for printed electronics expected to reach $300 billion over the next 20 years, research into better ways to print electronic devices for applications such as energy storage, photovoltaics, flexible electronics, transistors, and RFID tags can provide information of considerable economic value. Polymers, graphene, and carbon nanotubes have been demonstrated in conductive inks, but silver-based conductive inks continue to be one the most widely used materials in printed electronics due to their oxidation resistance, water dispersibility, and low resistivity. Given the importance silver nanostructures in printed electronics, we first attempt to address the following questions in Chapter 2: 1) what silver nanostructures result in the most conductive inks when deposited to form a thick film, and (2) how does the morphology and resistivity of these films depend on sintering temperature. We find that, compared to the same mass of silver nanoparticles (Ag NPs) and silver microflakes (Ag MFs), silver nanowires (Ag NWs) have the lowest resistivity when deposited from water and simply dried at low temperatures (70 °C).

Using this result that nanowires provide the best conductivity for thick films of silver deposited at low temperatures, in subsequent chapters we attempt to make the
case for the use of nanowires in a particular subset of printed electronics: thin film transparent conductors. Specifically we explore the use of low cost, abundant, and conductive copper nanowires (Cu NWs) synthesized and deposited from solution as replacements for indium tin oxide (ITO) and Ag NWs. We are motivated by the fact that, of the various alternatives to ITO, only metal nanowires are both solution coatable and achieve performance equivalent to ITO (Table 1). In addition, metal nanowire films are not only much more flexible than ITO, but can even be made to be stretchable.\textsuperscript{12-17} Thus metal nanowire films are currently the most promising material yet for replacing ITO across a broad range of existing and emerging applications. In Chapter 3 theoretical calculations of the junction resistance between Cu NWs are compared with experimental results to determine the optimum Cu NW aspect ratio necessary for optoelectronic properties equivalent to that of ITO and Ag NWs. Finally, Chapter 4 describes several methods of preparing core-shell Cu NWs for oxidation resistant transparent conductors and rendering them conductive without the use of high temperature annealing in an effort to address the major hurdles preventing the widespread use of Cu NWs in printed electronics. Brief introductions precede each Chapter and Chapter Sections. Chapter 5 summarizes the experimental methods corresponding to each previous Chapter.
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<thead>
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<th>TC Materials</th>
<th>Solution Coatable</th>
<th>ITO Level Performance</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doped Metal Oxides</td>
<td>No</td>
<td>Yes</td>
<td>Al:ZnO(^{19})</td>
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<td></td>
<td></td>
<td></td>
<td>Ga:ZnO(^{20})</td>
</tr>
<tr>
<td>Metal Thin Films</td>
<td>No</td>
<td>No</td>
<td>Au, (^{21})Ag, (^{22})Ni, Cr(^{23})</td>
</tr>
<tr>
<td>Metal Nanogrids</td>
<td>No</td>
<td>Yes</td>
<td>Au, Ag, Cu(^{13,24})</td>
</tr>
<tr>
<td>Electrospun Nanofibers</td>
<td>No</td>
<td>Yes</td>
<td>Cu(^{25})</td>
</tr>
<tr>
<td>Conductive Polymers</td>
<td>Yes</td>
<td>No</td>
<td>PEDOT:PSS(^{26-27})</td>
</tr>
<tr>
<td>Carbon Nanotubes</td>
<td>Yes</td>
<td>No</td>
<td>(^{28-30})</td>
</tr>
<tr>
<td>Graphene Flakes</td>
<td>Yes</td>
<td>No</td>
<td>(^{31-32})</td>
</tr>
<tr>
<td>Metal Nanowires</td>
<td>Yes</td>
<td>Yes</td>
<td>Ag, (^{33})Cu(^{34})</td>
</tr>
</tbody>
</table>

1.2 Background

Transparent conductors are a necessary component in flat-panel televisions, e-readers, smart-phones, smart-glass, touch-screens, organic light emitting diodes (OLEDs), and organic photovoltaics (OPVs).\(^{35}\) Indium tin oxide (ITO) is the most commonly used transparent conductor, with sales of approximately $1.6 billion in 2013, or 93% of the entire market for transparent conductors.\(^{36}\) The high transmittance (>90%) of ITO at low sheet resistances (10 Ω sq\(^{-1}\) on glass) is the primary reason for the
popularity of ITO. However, there are several attributes of ITO that are undesirable. ITO is a ceramic, and is thus brittle and prone to cracking. The abundance of indium in the earth’s crust is low (0.05 ppm), and its cost is correspondingly high, approximately $600 kg\(^{-1}\). However, for a 100 nm-thick film of ITO, only approximately 2% of the cost can be attributed to the cost of raw indium. Much of the cost of ITO film comes from the slow (linear coating rate of ca. 0.01 m s\(^{-1}\)), vapor phase sputtering process, which ensures that the cost of overhead per unit length of ITO film is high. In addition, more than 70% of the ITO sputtered from a target ends up on the walls of the sputtering chamber, from which it must be removed and recycled. Besides the need for a recycling infrastructure that does not add value, a major disadvantage of the sputtering process is that the rate of film throughput decreases with increasing film thickness, which makes thicker, high-conductivity ITO more expensive than low-conductivity ITO. Typical costs for ITO range from $5.5 \text{m}^{-2}$ for 150 Ω sq\(^{-1}\) ITO, up to $26 \text{m}^{-2}$ for 10 Ω sq\(^{-1}\) ITO. The thickness-limited throughput of ITO is especially problematic for OLEDs and organic photovoltaics (OPVs), which predominantly utilize ITO as the transparent conductor portion of the stack, due to the need for these devices to carry higher currents, and thus use relatively expensive ITO with a low sheet resistance (ca. 10 Ω sq\(^{-1}\)). For an OPV, ITO on polyethylene terephthalate (PET) can represent up to 51% of the materials cost. In addition it’s been noted that a solar energy conversion system cannot cost much more than \(\sim 10\) times the cost of paint, or \(\sim \$10 \text{m}^{2}\), if it is to be cost-competitive with fossil
fuels.\textsuperscript{41-42} However, indium tin oxide (ITO), the transparent conductor used for solution-coatable OPVs, by itself costs between $20 - $90 m\textsuperscript{-2}.\textsuperscript{43} Making the cost of OPVs and competitive with fossil fuels will require transparent conductive paint that costs \textasciitilde 10 times less than ITO.

In contrast to vapor-phase coating processes, the speed of a solution-phase coating process does not necessarily have to decrease with increasing coating thickness.\textsuperscript{44} Solution-phase coating processes also have lower capital and maintenance costs than sputtering.\textsuperscript{40, 45} These facts have motivated the search for alternatives to ITO that can be deposited from liquids at linear coating rates >100 times faster (>1 m s\textsuperscript{-1}) than the ITO sputtering process, but achieve the same or better transmittance and sheet resistance values. 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),\textsuperscript{28, 37} graphene,\textsuperscript{31, 46} and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS),\textsuperscript{27, 47} but only metal nanowires can be coated from solution and demonstrate performance comparable to ITO.\textsuperscript{18, 33-34} Ag NWs have become the most promising ITO alternative since silver is the most conductive metal and the Ag NWs are conductive after coating and do not oxidize under ambient conditions. This is possible
by first growing metal nanowires in a scalable, solution-phase synthesis, transferring the nanowires into a coating medium, and coating the nanowires onto a transparent substrate. Cambrios Technologies Corporation, building upon a Ag NW synthesis developed in the lab of Prof. Younan Xia and licensed from the University of Washington, has refined and improved the synthesis, purification, and coating of Ag NWs to obtain films with a transparency of 95% at 20 $\Omega$ sq$^{-1}$. Even though silver (approximately $\$765$ kg$^{-1}$) is more costly than indium (approximately $\$600$ kg$^{-1}$), Ag NWs can be deposited from solution with low-cost, roll-to-roll slot die coating. Due to their lower processing costs, Ag NWs are being increasingly used as the transparent electrode in touch sensors for computers sold by LG and Lenovo.

Copper on the other hand is only 6% less conductive than silver ($\rho_{\text{Cu}} = 1.68 \times 10^{-8}$ $\Omega$ m, $\rho_{\text{Ag}} = 1.59 \times 10^{-8}$ $\Omega$ m) but is more than 100 times cheaper and 1000 times more abundant. These factors make 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 nanowires together to render the films conductive, but this method is not convenient, and does not inhibit future copper oxidation.

My work over the past four years has been primarily to implement nanowires into printed electronics, predominantly Cu NWs as transparent conductors. Several
problems that were addressed include the proper shape and aspect ratio required to maximize conductive thick film and thin film electronic performance, the effect of nanowire-nanowire contacts in a Cu NW transparent conductor and the subsequent effect on optoelectronic performance of the entire network, exploring a solution phase method for rendering Cu NWs conductive that does not require annealing under H₂, and protecting Cu NW films from oxidation using both electrodeposition and electroless techniques. This thesis will discuss the results related to these problems in turn. It is my hope that this work will contribute to the knowledge concerning printed electronics and further motivate searches for ITO and Ag NW alternatives and replacements in the context of transparent conductors.
2. The Effect of Morphology on the Electrical Resistivity of Silver Nanostructure Films\textsuperscript{52}

Printed electronics based on conductive inks predominantly rely on thick films composed of silver since it is the most conductive metal and does not oxidize. Although silver nanowires (Ag NWs),\textsuperscript{53-56} silver nanoparticles (Ag NPs),\textsuperscript{57-65} and silver microflakes (Ag MFs)\textsuperscript{66-68} have all been deposited from a variety of solutions to create printed lines with high conductivities, the solutions used to deposit these nanostructures and the temperatures used to anneal them vary from paper to paper (see Table 2). By using only water to deposit these various nanostructures, and by annealing them across a range of temperatures, we sought to obtain a more complete and conclusive understanding of the relationship between morphology, temperature, and resistivity.
Table 2. Summary of literature values the resistivity of Ag NW, Ag NP, and Ag NF films (IPA = isopropanol, EG = ethylene glycol, HEC = hydroxyethyl cellulose, 2BE = 2-butyl ethanol).

<table>
<thead>
<tr>
<th>Shape</th>
<th>Dimensions (shortest, longest)</th>
<th>Drying Temp. (°C)</th>
<th>Resistivity (Ω cm)</th>
<th>Ink Solution</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW</td>
<td>60 nm, 15 μm</td>
<td>50</td>
<td>2.6 × 10⁻⁵</td>
<td>Water</td>
<td>53</td>
</tr>
<tr>
<td>NW</td>
<td>55 nm, 2.2 μm</td>
<td>110</td>
<td>1 × 10⁻³</td>
<td>IPA + stabilizers</td>
<td>56</td>
</tr>
<tr>
<td>NW</td>
<td>100 nm, 5-10 μm</td>
<td>250</td>
<td>2.1 × 10⁻⁵</td>
<td>EG</td>
<td>54</td>
</tr>
<tr>
<td>NW</td>
<td>48 nm, 6.2 μm</td>
<td>70</td>
<td>5.7 × 10⁻⁵</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150 nm, 27 μm</td>
<td>70</td>
<td>9.8 × 10⁻⁶</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>NP</td>
<td>≤ 50 nm, -</td>
<td>320</td>
<td>1.1 × 10⁻⁴</td>
<td>Water based ink</td>
<td>63</td>
</tr>
<tr>
<td>NP</td>
<td>46 nm, -</td>
<td>250</td>
<td>2.4 × 10⁻⁵</td>
<td>Water</td>
<td>61</td>
</tr>
<tr>
<td>NP</td>
<td>40 nm, -</td>
<td>180</td>
<td>5 × 10⁻⁶</td>
<td>Organic based ink</td>
<td>60</td>
</tr>
<tr>
<td>NP</td>
<td>12.2 nm, -</td>
<td>250</td>
<td>4.5 × 10⁻⁶</td>
<td>Ethanol based solvents</td>
<td></td>
</tr>
<tr>
<td>NP</td>
<td>400 nm</td>
<td>200</td>
<td>4.34 × 10⁻⁶</td>
<td>Ethanol and HEC</td>
<td>69</td>
</tr>
<tr>
<td>NP</td>
<td>40 nm, -</td>
<td>180</td>
<td>3.7 × 10⁻⁶</td>
<td>Water and EG</td>
<td>65</td>
</tr>
<tr>
<td>NP</td>
<td>12 nm, -</td>
<td>250</td>
<td>3.8 × 10⁻⁶</td>
<td>Tetradecane</td>
<td>64</td>
</tr>
<tr>
<td>NP</td>
<td>27 nm, -</td>
<td>400</td>
<td>2.4 × 10⁻⁵</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>-, 35 nm</td>
<td>200</td>
<td>9.4 × 10⁻⁶</td>
<td>EG and 2BE</td>
<td>66</td>
</tr>
<tr>
<td>NF</td>
<td>30 nm, 517 nm</td>
<td>200</td>
<td>7.4 × 10⁻⁶</td>
<td>Ethanol</td>
<td>68</td>
</tr>
<tr>
<td>NF</td>
<td>51 nm, 1.6 μm</td>
<td>250</td>
<td>9.3 × 10⁻⁵</td>
<td>Water</td>
<td></td>
</tr>
</tbody>
</table>

All four of the morphologies studied here were synthesized via literature methods. After syntheses, the nanowires, nanoparticles, and nanoflakes (Figure 1 shows XRD spectra of each morphology) were stored in distilled water and eventually deposited from these aqueous solutions into wells of known dimensions on a glass slide.
Since the concentration of silver was known for each shape, the same amount of silver by mass was deposited into each well. The various shapes were then heated at 70 °C for 10 minutes to remove any moisture and then separately placed in a tube furnace at 200 °C, 250 °C, 300 °C and 400 °C for 30 minutes. The sheet resistance was measured after the samples cooled to room temperature and resistivity values were then calculated.

![XRD patterns](image)

**Figure 1.** XRD patterns for the synthesized nanomorphologies.

This mass of deposited silver and the measured sheet resistance of the films were used to calculate resistivity with the following equation:

\[
\rho = R_s \frac{m}{d \times t^2}
\]
where \( \rho \) is the resistivity of the film, \( R_s \) is sheet resistance, \( m \) is the mass of silver species, \( \rho_{Ag} \) is the density of silver, and \( r \) is the radius of the well (assuming cylindrical shape). We note that some other publications determine the resistivity of the film with the following equation:

\[
\rho = R_s t^2 \]

where \( t \) is the film thickness measured with a profilometer or SEM. We chose not do to it this way for three reasons. First, given the natural roughness of the silver films, the determination of mass in a film can be made to a greater precision than the determination of the film thickness. Second, we are principally interested in the film resistance as a function of silver mass since we believe more people are interested in minimizing the mass of silver used to achieve a given line resistance and generally do not seek to minimize the thickness of a printed line necessary to achieve a given resistance. Third, different nanostructures will lead to very different film thickness given the same mass of silver. For example, the thickness of the silver nanoparticle films are less than half that of the silver nanowire films of the same mass, meaning that the silver nanowire films have roughly twice the porosity (Table 3 shows the experimental thicknesses of the films determined via profilometer). Obviously, the Ag NW films do not have twice the amount of silver, so it does not make sense to use the thicknesses of these two films to compare their resistivities. Thus we used the mass of silver in the
films discussed here to calculate an effective thickness, and used this thickness to determine the resistivity of the films.

Table 3. Thickness and root mean square surface roughness (Rq) of the silver nanostructures after heating at various temperatures.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Short Ag NWs (μm), Rq (μm)</th>
<th>Long Ag NWs (μm), Rq (μm)</th>
<th>Ag NPs (μm), Rq (μm)</th>
<th>Ag NFs (μm), Rq (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>3.6, 0.3</td>
<td>9.2, 1.2</td>
<td>3.0, 0.7</td>
<td>6.3, 1.1</td>
</tr>
<tr>
<td>200</td>
<td>2.5, 0.9</td>
<td>9.7, 1.6</td>
<td>3.7, 1.0</td>
<td>4.4, 1.2</td>
</tr>
<tr>
<td>250</td>
<td>3.5, 0.9</td>
<td>12.5, 3.9</td>
<td>3.4, 1.0</td>
<td>4.3, 1.1</td>
</tr>
<tr>
<td>300</td>
<td>1.2, 0.19</td>
<td>6.8, 1.1</td>
<td>3.9, 1.2</td>
<td>2.3, 0.5</td>
</tr>
<tr>
<td>400</td>
<td>1.2, 0.3</td>
<td>2.6, 0.75</td>
<td>3.7, 0.8</td>
<td>3.6, 1.1</td>
</tr>
</tbody>
</table>

2.1 Silver Nanostructure Morphology Change as a Function of Temperature

Figure 2 depicts SEM images of short Ag NWs (length = 6.2 ± 2.4 μm, diameter = 48 ± 10 nm) before and after annealing. Before annealing at high temperature there was no visible sintering between the nanowires (Figure 2A). However, once the short nanowires were subjected to 200 °C (Figure 2B) sintering at the contact points between nanowires could be observed. When the annealing temperature was increased to 250 °C, nanowires began to deform into particles due to Rayleigh instability (Figure 2C). At 300 °C the short nanowires have completely lost their initial morphology and melted into a film of silver (Figure 2D).
Figure 2. SEM of short Ag NWs (length = 6.2 ± 2.4 μm, diameter = 48 ± 10 nm) after (A) removal of water at 70 °C for 10 minutes and sintering at (B) 200 °C, (C) 250 °C, and (D) 300 °C for 30 minutes.

Junction resistance between nanowires in a network has been considered the limiting factor in the overall conductivity of a nanowire-based transparent conductor. Limiting the number of junctions in a film of a given mass requires longer nanowires. To examine this phenomenon in dense films of nanowires, we made films from Ag NWs with an average length = 27 ± 12 μm (diameter = 150 ± 30 nm) for comparison with the films made from the shorter Ag NWs with an average length of 6.2 ± 2.4 μm (see Figure 3 for dark field optical microscopy images of the short and long Ag NWs). Figure 4 shows the morphology of the long Ag NWs before (Figure 4A) and after annealing. At
200 °C (Figure 4B) the long Ag NWs exhibited junction formation similar to the short Ag NWs, albeit to a lesser extent. At 250 °C (Figure 4C) the long Ag NWs maintain their cylindrical shape with some slight curvature along the length of some nanowires due to the onset of Rayleigh instability. The difference between the long and short nanowires was even more apparent at 300 °C (Figure 4D) as the long Ag NWs clearly still resembled nanowires, even though they were significantly more distorted, in contrast with the short Ag NWs which completely melted under these conditions. This difference was due to the larger diameter of the long Ag NWs; the temperature required for spheroidization of nanowires due to Rayleigh instability increases with nanowire diameter.\textsuperscript{70, 76} This instability is dependent on surface diffusion, and because there is a higher ratio of surface atoms on the smaller diameter Ag NWs, they break apart into spheres at a lower temperature. For example, Langley \textit{et. al.}\textsuperscript{70} showed that transparent films of Ag NWs with diameters of 25 nm lost conductivity (broke into spheres) at 225 °C, but Ag NWs with diameters of 117 nm did not do so below 275 °C.

![Figure 3. DFOM images of (A) short Ag NWs and (B) long Ag NWs.](image)

\textsuperscript{70} Langley \textit{et. al.}\textsuperscript{70} showed that transparent films of Ag NWs with diameters of 25 nm lost conductivity (broke into spheres) at 225 °C, but Ag NWs with diameters of 117 nm did not do so below 275 °C.
Figure 4. SEM of long Ag NWs (length = 27 ± 12 μm, diameter = 150 ± 30 nm) after (A) water removal at 70 °C for 10 minutes and sintering at (B) 200 °C, (C) 250 °C, and (D) 300 °C for 30 minutes.

Figure 5 shows the effects of annealing on dense films of Ag NPs (average particle size = 27 ± 8 nm). After drying at 70 °C for 10 min (Figure 5A), no evidence of sintering between the Ag NPs was observed. At 200 °C (Figure 5B) and 250 °C (Figure 5C) the nanoparticles clearly started to melt and form conductive junctions required for efficient electrical percolation. The insets in Figures 5B and 5C are at the same scale as Figure 2A and offer an even better comparison of sintering before and after high temperature annealing where a change in morphology from single particles to large droplets is evident. At 300 °C the Ag NPs formed an even more connected network with
less distinct contacts between nanoparticles. The fact that the Ag NPs melt sooner than any of the Ag NWs is again expected considering their smaller diameter and greater radius of curvature which results in greater surface diffusion.

![Figure 5. SEM of Ag NPs (diameter = 27 ± 8 nm) after (A) water removal at 70 °C for 10 minutes, sintering at (B) 200 °C, (C) 250 °C, and (D) 300 °C for 30 minutes.](image)

Finally, Ag MFs (length = 1.6 ± 0.3 μm, thickness = 51 ± 8 nm) underwent identical annealing treatments as the previous silver shapes. Figure 6A shows the random orientation of the flakes in the film after drying at 70 °C. At 200 °C (Figure 6B) and 250 °C (Figure 6C) significant necking began to occur between nanoparticles and the smaller, sharper corners of the Ag NFs. At 300 °C (Figure 6D) the Ag NFs themselves
began to melt and deform, but sintering between the stacked faces of the flakes was not observed. Instead, flakes melted along their edges, and this did not appear to greatly enhance the interfacial contact between particles.

![Figure 6](image)

**Figure 6.** SEM of Ag NFs (length = 1.6 ± 0.3 μm, thickness = 51 ± 8 nm) after (A) water removal at 70 °C for 10 minutes, sintering at (B) 200 °C, (C) 250 °C, and (D) 300 °C for 30 minutes.

### 2.2 Silver Nanostructure Resistivity Change as a Function of Temperature and change in Morphology

The morphological changes of the silver nanostructures associated with an increase in annealing temperature can be directly correlated to the change in resistivity of the films as a function of temperature (Figure 7). After deposition from water and
drying at 70 °C for 10 minutes, all of the morphologies were conductive. However, films of the Ag NWs were orders of magnitude more conductive than nanoparticles or nanoflakes. The resistivity of the Ag NW films (1.76 × 10⁻⁵ Ω cm) was only 10 times that of bulk silver (ρ = 1.6 × 10⁻⁶ Ω cm). This is the lowest resistivity for Ag NWs deposited from water and dried at low temperatures (< 100 °C). The short Ag NWs were also quite conductive prior to annealing (ρ = 5.71 × 10⁻⁵ Ω cm) but slightly less so than the long Ag NWs. It’s likely this difference was due to the fact that electrons must traverse a larger number of nanowire-nanowire contacts in films of short nanowires. The junction resistance has previously been shown to dominate the resistivity of nanowire-based transparent conductive films. Here we are seeing that the junction resistance dominates the resistivity of thick films of nanowires as well, at least prior to sintering.
Figure 7. Resistivity versus sintering temperature for various silver nanomorphologies. See Table 4 for tabulated values.

Table 4. Resistivity values, calculated by mass ($\rho_m$) and thickness ($\rho_t$), of the silver nanostructures after heating at various temperatures.

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>Short Ag NWs</th>
<th>Long Ag NWs</th>
<th>Ag NPs</th>
<th>Ag NFs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_m$ ((\Omega) cm)</td>
<td>$\rho_t$ ((\Omega) cm)</td>
<td>$\rho_m$ ((\Omega) cm)</td>
<td>$\rho_t$ ((\Omega) cm)</td>
</tr>
<tr>
<td>70</td>
<td>$5.71 \times 10^{-5}$</td>
<td>$1.76 \times 10^{-5}$</td>
<td>$7.51 \times 10^{-2}$</td>
<td>$9.46 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$9.47 \times 10^{-5}$</td>
<td>$6.57 \times 10^{-5}$</td>
<td>$9.13 \times 10^{-2}$</td>
<td>$2.41 \times 10^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>$2.88 \times 10^{-5}$</td>
<td>$1.42 \times 10^{-5}$</td>
<td>$6.07 \times 10^{-5}$</td>
<td>$1.40 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$2.92 \times 10^{-5}$</td>
<td>$5.59 \times 10^{-5}$</td>
<td>$9.10 \times 10^{-5}$</td>
<td>$2.50 \times 10^{-4}$</td>
</tr>
<tr>
<td>250</td>
<td>$2.15 \times 10^{-5}$</td>
<td>$1.56 \times 10^{-5}$</td>
<td>$3.58 \times 10^{-5}$</td>
<td>$9.28 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$3.05 \times 10^{-5}$</td>
<td>$7.92 \times 10^{-5}$</td>
<td>$4.92 \times 10^{-5}$</td>
<td>$1.62 \times 10^{-4}$</td>
</tr>
<tr>
<td>300</td>
<td>$2.00 \times 10^{-5}$</td>
<td>$2.74 \times 10^{-5}$</td>
<td>$2.93 \times 10^{-5}$</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$9.71 \times 10^{-6}$</td>
<td>$7.54 \times 10^{-5}$</td>
<td>$4.63 \times 10^{-5}$</td>
<td>$3.78 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>$9.77 \times 10^{-6}$</td>
<td>$4.56 \times 10^{-4}$</td>
<td>$2.37 \times 10^{-5}$</td>
<td>$1.97 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$4.75 \times 10^{-6}$</td>
<td>$4.80 \times 10^{-4}$</td>
<td>$3.55 \times 10^{-5}$</td>
<td>$2.87 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
After annealing at 200 °C the resistivities of each morphology decreased by various amounts due to sintering of the contacts between the nanostructures. Once again the long Ag NWs exhibited the lowest resistivity ($\rho = 1.42 \times 10^{-5} \Omega \text{ cm}$), but now the short Ag NWs were only about half as conductive ($\rho = 2.88 \times 10^{-5} \Omega \text{ cm}$). The relative degrees to which the Ag NWs became more conductive after annealing is likely due to a greater degree of sintering between the short nanowires. The resistivity decrease for the Ag NPs ($\rho = 6.07 \times 10^{-5} \Omega \text{ cm}$) and Ag NFs ($\rho = 1.4 \times 10^{-5} \Omega \text{ cm}$) is much more dramatic compared to the nanowires. Examining Figures 5B and 6B, one can attribute this drop to the melting of particles into larger shapes and the necking between flakes, both of which decrease the resistivity of contact points throughout the films.

The relative resistivities of the films ($\rho_{\text{Long Ag NWs}} < \rho_{\text{Short Ag NWs}} < \rho_{\text{Ag NPs}} < \rho_{\text{Ag MFs}}$) did not change when the annealing temperature was increased to 250 °C. At this point all the values converged to be within the same order of magnitude. The Ag NPs and Ag NFs both become slightly more conductive ($3.58 \times 10^{-5} \Omega \text{ cm}$ and $9.28 \times 10^{-5} \Omega \text{ cm}$, respectively) due to further sintering at contacts. The Ag NFs have a slightly higher resistivity since contacts between flakes are only being made at the edges of flakes, whereas the Ag NPs sintered into a porous network. The resistivity of short Ag NW films decreases slightly from 200 °C to 250 °C ($2.88 \times 10^{-5} \Omega \text{ cm}$ to $2.15 \times 10^{-5} \Omega \text{ cm}$) while the long Ag NWs remain at roughly the same level (the increase in resistivity from $1.42 \times 10^{-5} \Omega \text{ cm}$ to $1.56 \times 10^{-5} \Omega \text{ cm}$ is within error). In Figures 2C and 4C both sets of
nanowires look as if they are beginning to transform into nanoparticles due to Rayleigh instability. The fact that this instability did not increase the resistivity of the films suggests that further sintering at contacts offsets any reduction in conductivity due to nanowire deformation.

At 300 °C, the short Ag NWs, long Ag NWs, and Ag NPs all exhibit resistivity values within error of one another: \( \rho_{\text{Short Ag NWs}} = 2.0 \times 10^{-5} \ \Omega \text{cm}, \rho_{\text{Long Ag NWs}} = 2.74 \times 10^{-5} \ \Omega \text{cm}, \) and \( \rho_{\text{Ag NPs}} = 2.93 \times 10^{-5} \ \Omega \text{cm}. \) The resistivities of the short Ag NWs and Ag NPs decrease slightly from their values at 250 °C due to almost complete melting of the silver to form a porous conductive sheet. The small increase in resistivity of the long Ag NWs was most likely due to continued melting and destruction of the nanowires, but their diameters are too large for the nanowires to melt completely to form a continuous porous film at 300 °C. Similarly, the Ag NFs begin to melt and lose their shape at this temperature, resulting in an apparent decrease in the number and extent of contacts between particles, and a decrease in conductivity (\( \rho = 4.06 \times 10^{4} \ \Omega \text{cm} \)).

Although 400 °C is a higher temperature than would be used in the majority of practical applications, it is instructive to observe what further changes in morphology and resistivity occurred. The short Ag NWs (Figure 8A) melted to form a continuous film of silver resulting in a resistivity of \( 9.77 \times 10^{-6} \ \Omega \text{cm} \) which is ~6 times the resistivity of bulk silver. The long Ag NWs (Figure 8B) continue to degrade without melting completely at this temperature, causing their resistivity to climb to \( 4.56 \times 10^{4} \ \Omega \text{cm} \). The
resistivity of the Ag NPs ($\rho = 4.56 \times 10^{-4} \ \Omega \ \text{cm}$) falls slightly from its value at 300 °C annealing, but remains within error as the nanoparticles melt and form an interconnected, porous film (Figure 8C). The film of Ag NFs become more conductive at 400 °C as the temperature was high enough to induce complete melting of the nanoflakes to form an interconnected network somewhat similar to, but more porous then, the film of Ag NPs.

![Figure 8. SEM images of (A) Short Ag NWs, (B) Long Ag NWs, (C) Ag NPs, and (D) Ag MFs sintered at 400 °C.](image)
Finally, we mixed Ag NPs with the long Ag NWs and sintered at 200 °C to see to what degree filling pore space and/or improving local sintering between nanowires with nanoparticles could improve the resistivity of this film. Figure 9A and 9B show films of 10:90 (mass ratio) Ag NPs:long Ag NWs before and after sintering at 200 °C. At this concentration the Ag NPs primarily cluster along the nanowires. While the resistivity of the 10:90 Ag NP:long Ag NW film dried at 70 °C is slightly higher than the film of just long Ag NWs at the same temperature ($7.4 \times 10^{-5} \, \Omega \, \text{cm}$ vs $1.76 \times 10^{-5} \, \Omega \, \text{cm}$ respectively), it is orders of magnitude lower than a film of pure, dried Ag NPs ($\rho = 7.51 \times 10^{-2} \, \Omega \, \text{cm}$) since there are less nanoparticle-nanoparticle contacts to lower the conductivity. Although sintering the films at 200 °C improves the resistivity slightly ($\rho = 3.1 \times 10^{-5} \, \Omega \, \text{cm}$), the melted Ag NPs do not assist in sintering at nanowire-nanowire contacts enough to lower the film resistivity below that of pure long Ag NWs. A similar result is seen when the Ag NP fraction is increased to 50 % in that the resistivity of the 50:50 films before ($4.2 \times 10^{-5} \, \Omega \, \text{cm}$) sintering (Figure 9C) is not below that of the pure long Ag NW films, but a large decrease in resistivity is seen when compared to the dried Ag NPs. After sintering at 200 °C ($\rho = 2.9 \times 10^{-5} \, \Omega \, \text{cm}$, Figure 9D) the resistivity is double the value for the pure long Ag NW films, but again lower than the pure Ag NP films. In this case the Ag NPs are still mostly clustering along the nanowires but fill the void areas between the nanowires to a greater degree than the 10:90 Ag NP:long Ag NW films. Finally, films of 90:10 Ag NPs:long Ag NWs were dried at 70 °C (Figure 9E) and sintered.
at 200 °C (Figure 9F). After drying, these films had a resistivity of $1.9 \times 10^{-4} \, \Omega \text{ cm}$, the highest of any of the mixtures due to the significant Ag NP portion. However, it is interesting to note that the addition of only 10% weight by mass of Ag NWs improved the conductivity of Ag NP films by almost three orders of magnitude, again highlighting the significance of the incorporation of a small fraction of high aspect ratio conductive material into a percolative network. This result is similar to previously observed effects of adding long nanowires to short nanowires in transparent conductive films.\textsuperscript{74, 77} When sintered at 200 °C, the 90:10 mixture has a resistivity of $7 \times 10^{-5} \, \Omega \text{ cm}$, almost identical to the pure Ag NP films at this temperature ($6.07 \times 10^{-5} \, \Omega \text{ cm}$).

We note that none of the resistivities of the mixed films are lower than the resistivity of a film of pure, long Ag NWs dried from solution at 70 °C, which we presume did not undergo any sintering. Thus we again conclude that a pure film of long nanowires is the best morphology for efficient electron transport at lower sintering temperatures due to the low number of internanoparticle contacts. No degree of pore-filling or additional sintering provided by nanoparticles offsets the poor electron transport through the partially sintered nanoparticle networks.
Figure 9. SEM images of 10:90 Ag NP:long Ag NW mixtures (A) dried at 70 °C and (B) sintered at 200 °C, 50:50 Ag NP:long Ag NW mixtures (C) dried at 70 °C and (D) sintered at 200 °C, and 90:10 Ag NP:long Ag NW mixtures (E) dried at 70 °C and (F) sintered at 200 °C.
3. Copper Nanowire Structure Property Relationship in the Context of Transparent Conductors

The above results suggest that, at the same mass of silver, Ag NWs provide the lowest resistivity both deposited from room temperature and sintered at higher temperatures due to the smaller amount of contacts between the nanostructures relative to other shapes. Transparent conductors, a subset of the printed electronics field, can also be fabricated from solution deposited Ag NW inks as an alternative to the expensive processing required for ITO thin films. As with thick films it is necessary understand the optimal shape Ag NWs should possess in order to manufacture transparent conductors with a higher transparency at lower sheet resistance. Not surprisingly, junction resistance along the Ag NW network has been shown to increase the overall resistance of the film as well.\textsuperscript{71-75} The impact of junction resistance requires transparent conductors to utilize longer nanowires to lower the number of contacts at the same areal density of nanowires. However, the Ag NWs must also have a small cross sectional area so as to scatter less light and increase the overall transparency of the film.\textsuperscript{18, 78} These results imply that an increase in Ag NW aspect ratio will increase the optoelectronic properties of thin film networks and have helped Ag NW films surpass the optoelectronic performance of ITO films.\textsuperscript{18, 79} Motivated by the fact that copper is 1000 $\times$ more abundant and 100 $\times$ cheaper than silver while only 6\% less conductive, we explored how junction resistance and film formation affect Cu NW thin film networks in an attempt to match Ag NW and ITO optoelectronic performance.
3.1 Effects of Length Dispersity and Film Fabrication on the Sheet Resistance of Copper Nanowire Transparent Conductors

While copper is a promising alternative to silver, Cu NWs have obstacles to overcome before their incorporation into transparent conductor applications can be realized. One main challenge is the propensity of copper to oxidize which results in increasing sheet resistance of transparent conductor devices, commonly attributed to the high contact resistance at nanowire–nanowire junctions due to the insulating copper oxide layers coating the nanowires that are clearly visible in TEM examinations of the nanowires. Reliable methods have been developed to remove the oxide surface layer on Cu NWs using either acetic acid washes or plasma cleaning in combination with high temperature hydrogen annealing.

The full impact of post-treatment on the performance of transparent conductors is difficult to assess because there are several materials and physical parameters that determine the electrical and optical properties of nanowire-based transparent conductors: nanowire conductivity, nanowire-nanowire contact resistance, nanowire areal coverage, and nanowire dimensions. A Monte Carlo model to extract contact resistance between nanowires, \( R_c \), and was modified to build pseudo-2D rod networks, where the thickness of the network is equal to the diameter of the rod. By comparing the experimental sheet resistance of well-characterized Ag NW samples the contact resistance was determined. Specifically, experimental sheet resistance data for transparent conductors of various nanowire areal coverage with Ag NWs of modest
aspect ratios (L/D = 200–275) and diameters of 50, 75, and 84 nm are in good agreement with the simulations. Moreover, the effective contact resistance between Ag NWs synthesized and fabricated in that manner was found to be 1.5–2.5 kΩ. Using an updated version of the model that incorporates polydisperse nanowire networks we then assessed the impacts of post treatments on $R_c$ for Cu NW networks deposited on PET. Several approaches are examined including repeated rinsing of the films in acetic acid, mechanical pressing, and plasma cleaning under forming gas (95% N2, 5%H2) and annealing in a hydrogen environment. The Cu NW transparent conductors are shown to have similar $R_c$ values as Ag NW-based TCs with similar dimensions.

Finally, in consideration that these post-treatment methods might remove nanowires from the substrate or alter their optical properties, we have developed a new characterization method for quantifying the area coverage of the nanowire transparent conductors using Rutherford Backscattering Spectrometry (RBS). Current techniques exist to measure the projected fractional area coverage of a surface by nanowires, $A_r$, such as processing many optical or SEM images of the nanowire network using programs like ImageJ or Clemex. This type of method suffers from poor statistics due to limited sampling areas, time-consuming data collection and analysis, and user subjectivity, which leads to limited reproducibility. All of these issues are exacerbated as the nanowire networks are spread over a larger area. A robust method that measures over a large area is necessary for reliable quantification of the area coverage. In one such
approach, Bergin et al. found a useful empirical relationship between $A_F$ and the optical transmittance of Ag NW films at $\lambda = 550$ nm.\textsuperscript{84} While the sample size is improved over the image analysis techniques, this approach could potentially suffer from unwanted changes in the transmittance measurements due to morphology modification of the Cu NW networks or the optical properties of the base substrate. In an effort to get around these issues, we propose that a new method using RBS may be used to measure $A_F$ for a nanowire TC more accurately by taking advantage of the elemental selectivity of RBS. In this approach the measurement of $A_F$ is based on the proportional relationship of the atomic areal density of the nanowires in a transparent conductor and the total signal yield attributed to the Cu NWs as measured by RBS.\textsuperscript{82,83}

### 3.1.1 Area coverage of Nanowire Networks in Transparent Conductors

The nanowire dimensions and areal coverage must be determined in order to apply the simulations of sheet resistance to experimental data and extract the effective contact resistance between Cu NWs. Measurements of $D$ yield a very tight distribution for all the nanowires in this study. Therefore, $D$ is measured for each nanowire batch and held constant in their respective simulations. As illustrated in Figure 10, the Cu NWs have positively skewed lengths. For each batch of nanowires a lognormal fit is applied to determine the mean length, $<L>$, and standard deviation, $\sigma$. These nanowire size characteristics ($D, <L>, \sigma$) are then incorporated into the simulations to give a more accurate representation of the real nanowire network. The number of rods in the
simulations is set by the areal coverage of nanowires as determined by our RBS method. RBS is widely used in the electronics industry to characterize the composition of thin films and the dopant concentration in silicon. Figure 11 shows RBS data for Cu NW films on PET substrates wherein the area under the curve in the counts versus energy plot increases with the copper content. The Cu NW transparent conductors were found to have area fractions ranging between 0.08 and 0.59. These $A_r$ values and those obtained from the optical transmittance method\textsuperscript{84} show good agreement (Figure 12) with less than 10% variation between the two methods in most cases. Notably, the measurements from the as-deposited Cu NWs (no post-treatments) show the greatest level of agreement, while the post-treated transparent conductors tend to deviate from RBS-measured values.
Figure 10. Histogram of CuNW lengths as measured by SEM. The distribution of lengths is fit with a lognormal distribution (black curve) with a mean length of 36.5 μm and a standard deviation of σ = 0.22. Inset: SEM image of CuNWs deposited on a PET substrate; scale bar is 10μm.
Figure 11. Representative RBS spectra for Cu NW transparent conductors, where the area fractions calculated from the RBS data are given in the legend. Note that the intensity of the copper peak scales with the area fraction as expected.
Figure 12. Comparison of area fractions measured using RBS versus area fractions obtained through transmission measurements (%T). Copper nanowires have an average aspect ratio $\langle L \rangle / \langle D \rangle = 330$. Post treatment nomenclature: AA: acetic acid washed four times; RT Press: pressed 80 bar for 1 minute at room temperature; PC/H2: plasma cleaned under forming gas and then annealed in H\textsubscript{2} rich environment at 175 °C for 30 minutes. The dotted lines denote a ±10% deviation from perfect agreement between the two methods (solid line).

The samples that were both plasma cleaned and pressed at room temperature showed the highest deviations. The optical transmission measurements apparently overestimate the area fraction in these samples. It may be due to the non-selectivity of the optical transmission method which is sensitive to contaminants left on the surface after post treatment that may scatter or absorb light. In contrast, RBS measures the copper content directly and is insensitive to the changes in nanowire shape,
contaminates, and residues. These data clearly demonstrate the feasibility of RBS to quantify areal coverage before and after post-processing without the ambiguities associated with relating optical transparency to nanowire coverage. Further, the RBS spot size is \( \sim 1 \) mm, so lateral uniformity of a nanowire film can be quantified. Area fractions of the nanowire transparent conductors reported in the remainder of this paper are measured with the RBS method.

**3.1.2 Effects of Post-Processing on Network Conductivity**

Figure 13 shows the measured sheet resistance for transparent conductor films on PET made with Cu NWs with \(<L>/D = 330\) and \(D = 76\) nm that underwent various post treatments. Note that Cu NW films with no post treatment or with only room temperature mechanical pressing are very highly insulating due to poor electrical contact primarily from the copper oxides present on the nanowires. Although the mechanical pressing technique enhances contact between the nanowires, it is still oxide to oxide contact, so oxide reduction methods are required for significant increases in the conductivity of the network. The acetic acid washes and plasma cleaning plus annealing approaches to reduce the contact resistance improve the conductivity of the films dramatically. When oxide removal measures were followed by room temperature pressing, the sheet resistances decreased slightly for area fractions \(<0.4\) and showed no change at higher area fractions. This is attributed to the scenario at low \(A_F\) where there are fewer nanowire-nanowire contacts, such that even relatively small improvements in
contact resistance between nanowires like that provided from pressing can have a significant effect on electrical percolation behavior of the transparent conductor.

**Figure 13.** Sheet resistance as a function of area fraction from Cu NW networks deposited on PET (points) and from simulations (solid line $R_c = 2k\Omega$, dashed line $R_c = 1k\Omega$). Four post-treatments were applied using one or more of the following as indicated in the legends: AA: acetic acid washed four times, RT Press: pressed 80 bar for 1 minute at room temperature, PC/H$_2$: plasma cleaned under forming gas and then annealed in a hydrogen rich environment at 175 °C for 30 minutes. Simulations use rod dimensions determined by SEM and fit with a lognormal distribution ($D = 76$ nm, $<L> = 330$ nm, $\sigma = 0.20$).

To quantify this comparison between post-processing methods $R_c$ values were extracted by fitting the experimental sheet resistance versus $A_F$ experimental data with a simulated curve using the $D, <L>$, and $\sigma$ for these nanowires and $A_F$ determined by RBS.
The four post treatments produce Cu NW networks that have similar effective contact resistances of $\sim 1$–2 kΩ. Notably, this is similar to the contact resistance range of 1.5–2.5 kΩ that was determined for Ag NW films composed of nanowires having diameters of 50, 84, and 75 nm, corresponding to nanowires with $L/D = 200$, 258, and 275, respectively. This provides further and compelling evidence that networks of Cu NWs can achieve similar levels of conductivity as networks composed of Ag NWs with comparable dimensions as long as steps are taken to remove oxides. Moreover, given the similarities of the sheet resistances and the optical performance after the four post treatments (Fig. 14), it is clear that the acetic acid treatment can replace the more expensive methods involving plasma cleaning and annealing in a hydrogen-rich environment.
Figure 14. Transmittance as a function of average sheet resistance for each of the Cu NW networks in this study. AA: acetic acid washed four times, RT Press: pressed 80 bar for 1 minute at room temperature, PC/H2: plasma cleaned under forming gas and then annealed in a hydrogen rich environment at 175 °C for 30 minutes.

3.2 A Rapid Synthesis of high Aspect Ratio Copper Nanowires for High-Performance Transparent Conducting Films

Although great improvements have been made in the performance of Cu NW films, they still do not match the performance of ITO. One way to improve the performance of nanowire films is to use nanowires with higher aspect ratios. Reduction of Cu(II) precursors in the presence of long-chain alkylamines produces high aspect ratio Cu NW’s (L/D = ~2500), but this synthesis takes several hours and must be performed under pressure. In comparison, production of copper nanowires by
reduction of Cu(II) with ethylenediamine (EDA) as a capping agent is several times faster, and can be performed at atmospheric pressure, making it more attractive for commercial production and mechanistic studies. However, the aspect ratio of Cu NW’s produced with EDA are typically lower ($L/D < 650$) than those produced by the alkylamine-based synthesis. Here, we detail the processes that lead to low aspect ratio nanowires in the EDA-based synthesis, and how to circumvent these processes to obtain nanowires up to 200 μm in length, and 35 nm in diameter ($L/D = 5700$).

In a typical synthesis, 10.5 - 20 μL of 35 wt% hydrazine ($N_2H_4$, 5.7 - 10.5 mM in the final solution) is injected into a mixture containing 4.8 mM of Cu(NO$_3$)$_2$, 14.3 M of NaOH and 72 - 214 mM of EDA preheated to 70 °C. When 10.5 mM of $N_2H_4$ is present, the Cu NWs grow with a uniform thickness of 35 nm prior to 16 min (Figure 15A). As the Cu NWs increase in length and yield, the solution becomes homogeneously dark red. The Cu NWs then spontaneously float to the air-water interface and start to turn pink at approximately 19 minutes. At this intermediate stage the surface of the nanowires becomes rough (Figure 15B), presumably due to the nucleation and growth of copper particles on the surface of the nanowires. At ~22 minutes, the Cu NWs form a pink-coloured cake at the surface of the solution, and have an average diameter of 154 nm (Figure 15C). The thicker NWs appear smoother than those at the intermediate stage. SEM images of nanowires at each stage of this process are given in Figure 16. Figure 15D shows that approximately 40% of the Cu(II) precursor is converted into thin nanowires.
at 16 min, and the remainder of the copper precursor adds to the sides of the nanowires over the next 6 minutes, resulting in a dramatic decrease in the nanowire aspect ratio.

**Figure 15.** TEM images of Cu NWs formed at the (A) early, (B) intermediate, and (C) final stages of a reaction. (D) Yield of reduced Cu as a function of reaction time. Note the average wire aspect ratio decreases over time.

**Figure 16.** SEM images of Cu NWs grown with 10.5 mM of N₂H₄, and collected at reaction times of (A) 14 min, (B) 19 min, and (C) 22 min, respectively.
The rapid conversion of the nanowires from thin to thick makes it impractical to obtain high aspect ratio nanowires by controlling the reaction time. Fortunately, this conversion can be prevented simply by lowering the concentration of N₂H₄. Figure 17 shows that Cu NW’s ~65 μm in length and ~35 nm in diameter (L/D = 1860) were obtained at 30 min by reducing the concentration of N₂H₄ from 10.5 to 5.7 mM. Running the reaction for longer times led to no appreciable increase in diameter (Figure 18). A slightly higher N₂H₄ concentration of 6.2 mM led to the formation of nanowires with particle-like structures along their length (Figure 19). Thus 5.7 mM represents the maximum concentration of hydrazine that does not cause the nanowires to increase in thickness. By lowering the reaction temperature to 60 °C, the average length of the Cu NWs can be increased to ~80 μm (L/D = 2280), with some wires as long as 200 μm (L/D = 5700), while retaining a diameter of ~35 nm (Figure 20).

Figure 17. Decreasing the concentration of N₂H₄ to 5.7 mM prevents thickening, resulting in nanowires (A) 63.4 ± 21.5 μm in length and (B) 34.4 ± 3.1 nm in diameter.
Figure 18. SEM images of Cu NWs collected at reaction times of (A) 30 min, and (B) 50 min show that running the reaction with a reduced amount of N2H4 (5.7 mM) prevents the increase in diameter observed at higher hydrazine concentrations.

Figure 19. Cu NWs with particle-like structures along their length formed at a N2H4 concentration of 6.2 mM after a reaction time of 30 min.
Figure 20. Dark field optical microscope (A) and SEM (B) images of Cu NWs synthesized at 60 °C with a length of 79.8 ± 30.6 μm (C) and a diameter of 36.1 ± 6.6 nm (D).

Previous EDA-based Cu NW syntheses have led to the production of Cu NWs with a distinctive tapered structure, in which the diameter of the nanowire increases from one end to the other.\textsuperscript{51, 89} Figure 21A shows a similar example of such a nanowire produced at an EDA concentration of 214 mM, for which the diameter increases from 32 nm near the seed to 155 nm at the end. This 6-fold increase in diameter over a length of 44 μm gives the nanowire an average $L/D = 460$. Thus, preventing the formation of this tapered structure is key to obtaining copper nanowires with high aspect ratios.
Fortunately, simply reducing the EDA to a lower concentration (95 mM) results in Cu NWs with thin, uniform diameters along their entire length (Figure 21B).

**Figure 21.** SEM images of (A) a 44 μm-long tapered Cu NW grown with 214 mM of EDA, and (B) a 33 μm-long taper-free Cu NW grown with 95 mM of EDA. Insets (scale bars, 200 nm) show a closer view of the different parts of the nanowires.

The tapered Cu NWs undergo a similar thickening process at higher N₂H₄ concentrations. Figure 22 shows tapered nanowires with particles on their sides at a N₂H₄ concentration of 6.2 mM, and tapered nanowires that grew radially to an average diameter of 195 nm at a N₂H₄ concentration of 10.5 mM. These experiments show the tapering and thickening phenomena are two independent processes. Figure 23 summarizes the processes of nanowire tapering and thickening.
Figure 22. Tapered Cu NWs also undergo (A) partial and (B) complete thickening at an N2H4 concentration of 6.2 and 10.5 mM, respectively.

Figure 23. Nanowire tapering and thickening processes. Red arrows represent the growth direction.

In order to gain additional insight into the reason for the formation of tapered nanowires, we monitored the growth of individual Cu NWs in real time with dark field optical microscopy. We note that this is the first real time observation of nanowire growth in solution. As shown in Figure 24, all the Cu NWs grow out of the seed particles on the substrate. This is consistent with the situation for Cu nanowires grown in a flask.\(^9\) When the concentration of EDA is low, the Cu NWs appear relatively long and thin (Figure 24A-C). In contrast, the Cu NWs become shorter, thicker and more tapered...
at higher concentrations of EDA (Figure 24D-F). Measurements of axial growth rates indicate that Cu NWs grow 3-4 times slower if the EDA concentration is increased from 95 to 214 mM (Figure 24G & 24H). This experiment shows the presence of additional EDA suppresses the axial growth of the Cu NWs, leading to a relatively greater amount of Cu added to the sides of the nanowire, and more tapering.

**Figure 24.** *In situ* visualization of Cu NW growth in the presence of 95 mM (A-C) and 214 mM of EDA (D-F). The growth rate, \( <G> \), of Cu NWs is (G) 63 ± 5 nm s\(^{-1}\) and (H) 18 ± 4 nm s\(^{-1}\), respectively.
To fabricate transparent conducting films of Cu NWs, we transferred the Cu NWs into a nitrocellulose-based ink solution and coated them onto a glass substrate with a Meyer rod. The plot of specular transmittance ($\%T$) versus sheet resistance ($Rs$) for the Cu NW networks is shown in Figure 25, along with some of the best previous literature results. The TCs made of long, thin Cu NWs ($L/D = 1860$) exhibit excellent performance in terms of transparency and conductivity. For example, at $\%T = 95\%$, the nanowire network has a $Rs$ below $100 \, \Omega \, sq^{-1}$, and it is only $3\%$ less transparent than ITO at a $Rs$ of $50 \, \Omega \, sq^{-1}$. Films made of higher aspect ratio Cu NWs ($L/D = 2280$) do not exhibit better performance. This may be due to the poly-disperse distribution of nanowire lengths, or the fact that high aspect ratio nanowires behave more like flexible filaments than rigid rods; additional modeling efforts may shed light on this issue. At $Rs = 100 \, \Omega \, sq^{-1}$, the $\%T$ of films made of the tapered Cu NWs ($L/D = 460$) drops to $92$-$93\%$. This result confirms the importance of controlling the aspect ratio of the nanowires by minimizing tapering.
Figure 25. %T vs. Rs of Cu NW networks based on high aspect ratio Cu nanowires (L/D = 2280, 1860) as well as tapered nanowires (L/D = 460). Comparison data are shown representing current state of the art transparent conductors, including Cu NWs (L/D = 330, 2500), carbon nanotubes (L/D = 1500), Ag NWs (L/D = ?, 600), and ITO.
4. Methods of Rendering Copper Nanowires Oxidation Resistant and Their Application in as Transparent Electrodes in Electronic Devices

Copper is 6% less conductive than silver, but it is 1000 times more abundant and 100 times less expensive.\textsuperscript{49-50} Thus, replacing Ag NWs with Cu NWs should offer comparable levels of performance at lower cost. One disadvantage of Cu NWs relative to Ag NWs is that they have a greater potential to oxidize, which reduces the conductivity of the film. Although films of Ag NWs can be heated in air to sinter them together at the contacts, and thereby reduce the contact resistance between nanowires, the fact that Cu NWs are covered with a layer of copper oxide prevents them from sintering together in air. Instead, it has been necessary to anneal Cu NW films under hydrogen in order for the films to obtain performance comparable to that of Ag NWs.\textsuperscript{34, 51, 89} Despite the lower cost of Cu NWs, this lack of stability and necessity of hydrogen annealing has hindered their wider use in practical applications.

The challenges associated with making Cu NW networks conductive and protecting them from oxidation are likely responsible for the fact that there are many articles exploring the use of Ag NWs as a replacement for ITO in solar cells,\textsuperscript{33, 93-97} but only one reported case prior to the section below on the use of solution-coated Cu NWs in an OPV.\textsuperscript{98} In that work, following hydrogen annealing of the Cu NW film, the nanowire electrode was planarized with PEDOT:PSS. The authors noted that the processing conditions had to be modified to prevent the degradation of the Cu NW film.
during coating of the acidic PEDOT:PSS suspension. The authors vacuum deposited the remaining layers onto this anode to create a bulk-heterojunction (BHJ) small-molecule organic solar cell with an efficiency of 3%. Although this work demonstrated that Cu NWs can be used as an anode in a solar cell, unprotected Cu NWs are clearly not well-suited for this purpose since they will gradually become non-conductive due to oxidation over a matter of months.99

In this chapter we describe a completely solution phase approach to rendering Cu NWs conductive as well as several methods of protecting the Cu NWs from oxidation. We also utilize the coated CuNi films as transparent conductors for OPVs.

4.1. Solution-Processed Copper-Nickel Nanowire Anodes for Organic Solar Cells81

4.1.1. Preparation of Conductive Copper Nanowire Films

Figure 26A depicts the dipping of a Cu NW film into glacial acetic acid to remove copper oxide and the nitrocellulose left over from the ink from which the nanowires were coated. This simple procedure was inspired by previous reports that acetic acid can selectively remove copper oxides from the surface of copper without etching the underlying copper.100 The experimental procedure described here has been optimized to minimize the resistance of the Cu NW film without damaging the nanowires or washing them off the substrate. Figure 26B and 26C show TEM images of the same Cu NW taken before and after acetic acid treatment. The 2-3 nm-thick layer of copper oxide present in 26B is absent following the acetic acid treatment, but the underlying Cu NW appears
unscathed. In addition to removing copper oxide, the glacial acetic acid removes nitrocellulose, the film former, from the substrate. The nitrocellulose can be observed as a white coating on the slide after the first dip in acetic acid. The white coating disappears after subsequent acetic acid dips, and remains as a residue in the beaker used for the acetic acid wash after the acetic acid evaporates.

Figure 26. (A) Cu NW film coated on a glass slide immersed in glacial acetic acid. TEM images of the same Cu NW (B) before and (C) after acetic acid treatment. (D) Plot of transmittance vs. sheet resistance for Cu NW films after annealing under H2 at 175 °C or after the acetic acid treatment.

Figure 26D compares the transmittance (%T, λ = 550 nm) and sheet resistance ($R_s$) of Cu NW films that underwent the acetic acid treatment with those that underwent the
plasma cleaning and annealing under H\textsubscript{2} at 175 °C. This comparison shows that the two methods obtain comparable film performance, with the H\textsubscript{2} annealing obtaining slightly better performance than the acetic acid treatment. We believe this difference is due to the fact that, while both methods eliminate copper oxides from the surface of the nanowire, the elevated temperature during H\textsubscript{2} annealing provides additional energy for the Cu NWs to sinter together and reduce contact resistance. Given that one would expect very little sintering to take place over the course of the acetic acid treatment, it is somewhat surprising that the acetic acid treatment can obtain values that are nearly equivalent to those obtained with annealing under H\textsubscript{2}.

Mechanical pressing of nanowire films has previously been shown to decrease the sheet resistance of a Ag NW network, presumably by increasing the contact area between nanowires, and decreasing the contact resistance.\textsuperscript{71, 98, 101-102} Thus it seems logical that the application of mechanical pressing after the acetic acid treatment might improve the performance of the electrode to be comparable to the performance of a Cu NW film annealed under H\textsubscript{2}. The SEM images in Figures 27A and 27B show there is no discernable difference in the morphology of the Cu NW film before and after acetic acid treatment. After pressing the wires at 80 bar for 1 minute (Figure 27C), the junctions between the nanowires appear to be fused together and the average surface roughness (Ra) decreases from 78 nm to 37 nm. However, a graph of %T vs. R\textsubscript{s} before and after pressing (Figure 27D) shows there is no improvement in performance after pressing.
This is due to the fact that both the sheet resistance and the transmittance of the film decrease after pressing. For example, for a Cu NW film treated with acetic acid with an initial sheet resistance of 89 $\Omega$ sq$^{-1}$ at 93 %$T$, the sheet resistance and transmittance decreased to 61 $\Omega$ sq$^{-1}$ and 91 %$T$ after pressing. The decrease in %$T$ is likely due to flattening of the nanowires during the pressing process, which increases the area coverage of the nanowires, and decreases the light transmitted through the open areas of the network. Indeed, the Cu NWs appear to be more cylindrical in Figure 27B, and somewhat more rectangular and flattened in Figure 27C. Lowering or increasing the applied pressure relative to 80 bar did not result in any improved optoelectronic performance (see Figure 28A). Figure 28B shows the flattening of the nanowires was more pronounced at 160 bar than at 80 bar.
Figure 27. SEM images of Cu NWs (A) as deposited, (B) washed with acetic acid, and (C) after pressing at 80 bar. (D) Plot of transmittance vs. sheet resistance of acetic acid washed Cu NW films before and after pressing.

Figure 28. (A) Plot of transmittance vs. sheet resistance of CuNW films treated with glacial acetic acid and pressed at various pressures. (B) SEM image of a Cu NW film pressed at 160 bar.
4.1.2. Electroless Nickel Plating

In order to protect the Cu NWs from oxidation, we have previously demonstrated the electroless plating of nickel onto the nanowires while they are dispersed in solution, as well as the electroplating of nickel onto the nanowires after they are deposited on a film. Electroplating Ni onto Cu NWs after film formation avoids laborious centrifugation and washing steps, eliminates ethylene glycol waste, and prevents the aggregation of NWs due to the magnetic attraction between CuNi NWs in solution. However, electroplating is somewhat more complicated in that it requires the use of a current source, and is difficult to apply uniformly over a large area due to the resistance of the nanowire film. Here we explore a third method, electroless plating of nickel onto copper nanowire films that offers the advantages of both previous methods with few of the disadvantages.

Following acetic acid treatment, the Cu NW electrodes were briefly dipped into an activation solution containing Pd\(^{2+}\) before being transferred to a nickel plating solution (Figure 29A). Activation of the surface of Cu with Pd has previously been shown to facilitate the plating of Ni onto a Cu surface. We see no plating of Ni onto the Cu NWs if they are not first exposed to Pd\(^{2+}\). Although Pd is not an abundant, inexpensive element, so little of the Pd is actually incorporated into the nanowires (0.00482 g m\(^{-2}\)) that the contribution of the cost of Pd to the cost of the nanowire films is
less than two orders of magnitude smaller than the cost of ITO film ( $0.13 \text{ per m}^2$, see Appendix).

**Figure 29.** (A) Cu NW film immersed in a nickel plating solution. (B) SEM image of CuNi NWs. Dark field optical microscope images of Cu NWs before (C) and after (D) Ni plating.

A linear relationship between the time spent in the nickel solution and the amount of nickel deposited on the Cu NW network is shown in Figure 30. After 12.5 minutes in the plating solution, the diameter of the resulting CuNi NWs increased from $67 \pm 15 \text{ nm}$ to $90 \pm 31 \text{ nm}$ (Figure 29B). Dark field optical microscope images of the nanowire network before and after 20 % nickel plating (Figures 29C & 29D) show that the color of the nanowires changed from reddish to grey. The nickel coating resulted in a
small decrease in sheet resistance, but about a 4% drop in the transmittance (at $\lambda = 550$ nm). This drop in transmittance is consistent with previous results, and is due to the increase in the diameter of the nanowires after nickel coating.\textsuperscript{99} Figure 31A shows a graph of transmittance ($\lambda = 550$ nm) versus sheet resistance before and after the nickel coating.

\begin{center}
\includegraphics[width=\textwidth]{image}
\end{center}

\textbf{Figure 30.} The mole percent of Ni plated onto the Cu NWs versus time in the plating solution.
A

Transmittance (%) vs. Sheet Resistance (Ω sq⁻¹)

B

$t_{12}$ (hrs) vs. Temperature (°C)

C

Sheet Resistance (Ω sq⁻¹) vs. Time (hours)

Legend:
- Black squares: Copper
- Red circles: 20% Ni
- Blue triangles: Silver
- Green triangles: 28% Ni
Figure 31. (A) Transmittance versus sheet resistance for Cu NWs before and after nickel plating. (B) Modified Arrhenius plot of the time required for the sheet resistance to double versus temperature for films of Cu, 20% CuNi, and Ag NWs. (C) Sheet resistance change over 24 hours for Cu NWs, CuNi NWs (20% and 28% Ni) under humid conditions (85 °C/85 RH).

Figure 31B shows coating the Cu NWs with 20% Ni gives them a resistance to oxidation comparable to Ag NWs. This plot shows the time required for the sheet resistance of nanowire films of comparable transmittance (85 – 87 %T) to double ($t_{1/2}$) after being placed in a dry oven heated to a given temperature (75-150 °C). For example, it takes about 1 hr for the sheet resistance of a Cu NW film to double at 105 °C, but this increases to 38 hrs if the NWs are coated with 20% Ni. The stability of the nanowire films was also compared in a humidity chamber at 85 °C and 85 ± 3% RH (Figure 31C). Under these conditions, Cu NW films became insulating in less than 1 hr, 20% CuNi NWs were stable for <5 hrs, and 28% CuNi NWs exhibited a stability similar to Ag NW films.

4.1.3. CuNi Nanowire Solar Cell Performance

One of the obstacles to the replacement of ITO with nanowire films in OPVs is the greater surface roughness of nanowire electrodes. The peak-to-valley surface roughness of nanowire electrodes coated from solution and treated with acetic acid (Figure 27B) is slightly less than two nanowire diameters, or 104 nm. This surface roughness is nearly the same as the thickness of a typical polymer active layer. As a result, many of the OPV devices made with nanowire electrodes have exhibited small shunt resistances, and correspondingly low OPV efficiencies.
One approach to making a smooth nanowire electrode involves transferring the nanowires from a donor substrate to a polymer, and in the process embedding them in the polymer.\textsuperscript{108} In one case, this was accomplished by spin coating a polymer (polyacrylate) over a film of Ag NWs, photocuring the polymer film, and peeling away the polymer film to reveal a smooth (root mean square roughness <5 nm) surface containing the nanowires embedded in the polymer film.\textsuperscript{107} The best device made with this method exhibited an efficiency of 3.28%.\textsuperscript{107} Peumans and co-workers achieved an efficiency of 4.2% by laminating Ag NWs into the surface of PEDOT:PSS.\textsuperscript{106} However, transferring the nanowires from one substrate to another is quite difficult to do with high fidelity, and may result in low device yields in a production environment.

We have found that comparable or greater device efficiencies can be achieved by optimizing the coating process for PEDOT:PSS over the nanowire film. We have previously obtained device efficiencies of 2.8% and 2.5% on glass and PET, respectively, by coating a Ag NW film with a single coating of PEDOT:PSS with a thickness of 40 nm.\textsuperscript{93} Since then, we have found that coating the nanowire film three times with PEDOT:PSS mixed with ethylene glycol and a fluorosurfactant allowed us to achieve device efficiencies nearly twice that of those obtained previously. As the current PEDOT:PSS coating is not much thicker than the ones used previously, we believe the reason for the increase in device efficiency from the three-step coating process is principally due to the fact that a more complete coating is achieved, thereby facilitating
the transport of holes to the metallic nanowires while preventing device shorts and
electron-hole recombination at the surface of the metal nanowires.

Figure 32A and 32B show AFM images before and after CuNi NWs were coated
with PEDOT:PSS. Prior to testing the CuNi NW electrodes in an OPV device, the films
were pressed (80 bar, 1 minute) in an attempt to decrease the roughness of the nanowire
network. A nickel concentration of 28 % was chosen to increase the resistance of the
nanowire film to oxidation. The $R_a$ of the pressed CuNi NWs dropped from 52 nm to 18
nm after coating PEDOT:PSS onto the nanowires.

![AFM images of Cu NW films (A) before and (B) coating with PEDOT:PSS.](image)

**Figure 32.** AFM images of Cu NW films (A) before and (B) coating with PEDOT:PSS.

Figure 33A is a schematic illustrating the layers of the finished device.
FTAZ:PCBM denotes the blend of PBnDT-FTAZ and PCBM used as the active layer.
This blend was chosen due to its previously demonstrated high performance in BHJ
OPVs utilizing nanowires as the transparent electrode. Films of Ag NWs (%$T = 76, R_s =
14 \ \Omega \ \text{sq}^{-1}$) and CuNi NWs (%$T = 80, R_s = 36 \ \Omega \ \text{sq}^{-1}$) were fabricated to have similar film
properties to determine if the replacement of Ag with the lower-cost CuNi NWs would
affect the performance of the OPV. Representative current–voltage curves for the devices are shown in Figure 33B and the relevant photovoltaic characteristics are summarized in Table 5. Compared to the ITO reference, both nanowire based devices display lower short-circuit currents ($J_{sc}; J$ at $V = 0$), lower fill factor (FF), and slightly lower open circuit voltages ($V_{oc}; V$ at $J = 0$), resulting in lower device efficiencies.

Figure 33. (A) Diagram of the nanowire-based FTAZ BHJ solar cell. (B) Characteristic J-V curves of solar cells with ITO, Ag NWs, and CuNi NWs as the transparent electrode. (C) The transmittance of the transparent conducting films and respective devices versus wavelength. (D) IPCE versus wavelength curves of the FTAZ BHJ solar cells with ITO, Ag NW, and CuNi NW anodes under one sun condition (100mW/cm2).
Previous papers also show that the $V_{OC}$ for OPVs using Ag NW films is lower than ITO films.\textsuperscript{93-95, 97} This has previously been attributed to the fact that Ag has a lower work function (4.3 – 4.7 eV)\textsuperscript{109-111} than ITO (4.7 – 5.0 eV),\textsuperscript{112-114} resulting in a greater barrier to the transport of holes out of the device.\textsuperscript{93} Compared to our previous work in which the $V_{OC}$ for OPVs using nanowire films as anodes was on average 59 % of those obtained for ITO, the three step coating process has improved the $V_{OC}$ to be 96% (Ag NWs) and 95% (CuNi NWs) that of the ITO reference. The slightly lower $V_{OC}$ observed for nanowire films may be due to the fact that the coverage of PEDOT:PSS on the nanowires is not as uniform and pinhole-free as the coating of PEDOT:PSS on ITO.

The lower $J_{SC}$ of the devices can be attributed to the lower transmittance of the Cu NW and Ag NW films relative to ITO. The $J_{SC}$ of the nanowire-based devices is roughly 20% lower than the ITO-based device, which is roughly equivalent to the difference in the percent of incident light absorbed by the nanowire and ITO-based devices (see Table 6 and Figure 33C). This inference is further supported by the correlation between the transmittance of the films and devices (Figure 33C) with the incident photon to current

### Table 5. Photovoltaic performance of the FTAZ BHJ solar cells.

<table>
<thead>
<tr>
<th>Anode</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>11.97</td>
<td>0.810</td>
<td>74.0</td>
<td>7.1</td>
</tr>
<tr>
<td>Ag NW</td>
<td>10.18</td>
<td>0.776</td>
<td>63.4</td>
<td>5.0</td>
</tr>
<tr>
<td>CuNi NW</td>
<td>9.98</td>
<td>0.767</td>
<td>63.5</td>
<td>4.9</td>
</tr>
</tbody>
</table>
efficiency (IPCE) of the devices (Figure 33D). Thus the $J_{sc}$ of the nanowire-based devices can likely be improved by improving the transmittance of the nanowire films at a given sheet resistance.\textsuperscript{95, 115}

Table 6. Film and Device Characteristics ($\lambda = 550$ nm).

<table>
<thead>
<tr>
<th>Anode</th>
<th>$R_s$ (Ω sq(^{-1}))</th>
<th>%$T$ of Film and Substrate</th>
<th>%$T$ of Device</th>
<th>% Light Absorbed by Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>20</td>
<td>88</td>
<td>10.6</td>
<td>77.4</td>
</tr>
<tr>
<td>Ag NW</td>
<td>14</td>
<td>67</td>
<td>4.3</td>
<td>62.7</td>
</tr>
<tr>
<td>CuNi NW</td>
<td>36</td>
<td>71</td>
<td>6.7</td>
<td>64.3</td>
</tr>
</tbody>
</table>

4.2. Copper Nanowire Networks With Transparent Oxide Shells That Prevent Oxidation Without Reducing Transmittance\textsuperscript{116}

Cu NWs are more sensitive to oxidation than Ag NWs, and this fact has hindered their use in applications. There have been a limited number of studies that aim to address the critical hurdle of protecting Cu NWs from oxidation. One earlier attempt to protect Cu NWs consisted of coating a layer of Ni onto Cu NWs dispersed in ethylene glycol at 120 °C with electroless plating.\textsuperscript{99} Films of cupronickel nanowires were 1000 times more resistant to oxidation than films of Cu NWs, but their transmittance was up to 10% lower than films of Cu NWs at a sheet resistance of 60 Ω sq\(^{-1}\).\textsuperscript{99} This decrease in transmittance was principally due to the fact that the nickel coating increased the diameter of the nanowires, which in turn increased the amount of light blocked by the nanowires at a given area coverage.\textsuperscript{78, 84, 117-118} In a separate recent report, a layer of aluminum-doped ZnO and Al\(_2\)O\(_3\) was deposited on electrospun copper nanofibers by
atomic layer deposition (ALD).\textsuperscript{119} This coating was able to prevent oxidation of the copper nanofibers while decreasing the transmittance of the film at a given sheet resistance by $\sim 1\%$. The main drawback of this approach is that ALD remains a fairly costly technique that is better suited to small-area, high-value devices than large-area, low-cost roll-to-roll production.\textsuperscript{120}

Here we report a solution-phase process for protecting films of Cu NWs from oxidation without degrading their performance. This general approach consists of electroplating a metal, such as Zn, Sn, or In, onto the surface of Cu NWs after film formation, followed by oxidation of the metal coating to create a transparent zinc, tin, or indium oxide shell. These oxide shells protect Cu NWs from oxidation without degrading the transmittance and conductivity of NW networks.

Cu NWs (>20 $\mu$m in length and $\sim 70 \pm 25$ nm in diameter) were synthesized in a manner similar to that reported previously and stored in an aqueous solution containing hydrazine (3 wt %) and polyvinylpyrrolidone (1 wt %).\textsuperscript{51} A thin, uniform film of the NWs was prepared on glass with a Meyer rod by following the procedure reported previously.\textsuperscript{51} The Cu NW film (65 mg m$^{-2}$) exhibited a sheet resistance of 32 $\Omega$ sq$^{-1}$ at a transmittance of 85% at $\lambda = 550$ nm (all transmittance values refer to specular transmittance). The sheet resistance and transmittance of a NW film can be varied by simply changing the areal density of the NWs.\textsuperscript{51}
The Cu NW network was coated with Zn by electroplating Zn(II) (1 mM ZnCl$_2$) in 0.1 M deaerated sodium acetate (pH $\sim$8.2) at room temperature. As shown in Figure 34A (red curve), the cyclic voltammetry (CV) profile of the Cu NW network in solution without Zn(II) is relatively featureless from $-0.25$ to $-1.0$ V vs NHE (normal hydrogen electrode). The current onset at $-1.0$ V is from background water reduction. Upon addition of 1 mM ZnCl$_2$ (blue curve), a redox couple was observed at $E_{p,c} = -1.08$ V and $E_{p,a} = -0.68$ V ($E_{p,c}$ and $E_{p,a}$ are the cathodic and anodic peak/plateau potentials, respectively). The CV behavior is consistent with the electrodeposition of Zn(0) and the reoxidation of Zn(0) during the forward and the reverse scans through Zn$^{II} + 2e^- \rightarrow$ Zn$^0$.

Continuous electroplating was conducted by holding the potential at $-1.15$ V, as shown in Figure 34B. Both the transmittance and sheet resistance of the NW networks decreased with increasing Zn content (Figure 34C). For later oxidation studies, we made a Cu–Zn core–shell (Cuc–Zns) NW network consisting of 39 mol % of Zn (electroplating time = 10 min), which exhibited a sheet resistance of 25 $\Omega$ sq$^{-1}$ and a transmittance of 76% at $\lambda = 550$ nm.

Figure 34. (A) CVs of a Cu NW network in 0.1 M deaerated sodium acetate (pH $\sim$8.2) with and without 1 mM ZnCl$_2$ added to the solution. Scan rate, 100 mV/s. (B) Current and Zn content of the film as a function of electroplating time at $-1.15$ V vs NHE with 1
mm ZnCl₂. (C) Plots of sheet resistance and transmittance at $\lambda = 550$ nm vs electroplating time at $-1.15$ V.

Figure 35 shows dark-field optical microscopy (DFOM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray energy-dispersive spectroscopy (EDS) images of the Cu NW and Cu–Zn (39 mol % of Zn) NW networks. The optical images in Figure 35A,B demonstrate that the Cu NWs are evenly dispersed across the glass substrate and interconnected. The color of light scattered from the NWs changes from reddish-orange to neutral gray upon coating with Zn. The electroplating of Zn occurred only on the surface of the Cu NWs, with no Zn deposited on the open areas of the substrate. This allowed the network to retain its transmittance after electroplating. The SEM images in Figure 35C,D further confirm that the electroplating occurred only on the surface of the Cu NWs. The surface roughness of the NWs increased after Zn coating, and the average diameter of the NWs increased from ~70 to ~100 nm. Similar observations were made by TEM images in Figure 35E,F. Cu and Zn have similar atomic masses and therefore do not exhibit much difference in contrast in TEM images. EDS mapping in Figure 35G shows the Cu NW is completely coated with a layer of Zn. The average thickness of the shell was determined to be $15 \pm 5$ nm after electrodeposition of ~39 mol % of Zn.
Unlike Ni coatings,\textsuperscript{99} the decrease in the transmittance upon coating of Zn can be recovered. When oxidized, ZnO and/or Zn(OH)$_2$ is transparent.\textsuperscript{121,122} Figure 36A shows that by dipping the Cu–Zns NW film in H$_2$O$_2$ (2 wt %), its transmittance gradually increased to 84.3\% after 15 min, a value close to that of the Cu NWs prior to Zn coating.

Figure 35. DFOM (A,B), SEM (C,D), and TEM (E,F) images of Cu (A,C,E) and Cu–Zns (39 mol \% of Zn) (B,D,F) NWs. (G) EDS mapping image of a Cu–Zns (39 mol \% of Zn) NW.
(85%), while its sheet resistance remained nearly unchanged. The fact that Zn was electroplated onto the Cu NW network after annealing ensures that the oxidation of the Zn shell does not result in the formation of oxide shells between Cu NWs at their point of electrical contact, and thus there is initially no increase in sheet resistance during the oxidation of Zn. Longer exposures to H$_2$O$_2$ resulted in a slight increase in the sheet resistance, potentially due to the oxidation of Cu NWs inside the oxide shell, or alternatively loss of the NWs from the substrate. These results are in contrast to the H$_2$O$_2$ treatment of Cu NWs in Figure 36B in which the sheet resistance of the bare Cu NWs increases rapidly after exposure to H$_2$O$_2$, exceeding 800 Ω sq$^{-1}$ after 15 min. The full transmittance spectra of films of both bare Cu NWs and Cu–ZnS NWs before and after H$_2$O$_2$ (2%) treatment for 15 min are shown in Figure 36C.
Figure 36. Plots of transmittance ($\lambda = 550$ nm) and sheet resistance of Cu–Zn$_x$ NWs (A) and Cu NWs (B) vs treatment time in a 2 wt % solution of $\text{H}_2\text{O}_2$ in H$_2$O. (C) Transmittance spectra for ITO (11 $\Omega$ sq$^{-1}$), Cu NWs (32 $\Omega$ sq$^{-1}$), Cu NWs after $\text{H}_2\text{O}_2$ treatment for 15 min (>800 $\Omega$ sq$^{-1}$), Cu–Zn$_x$ NWs (25 $\Omega$ sq$^{-1}$), and Cu–Zn$_x$ NWs after $\text{H}_2\text{O}_2$ treatment for 15 min (29 $\Omega$ sq$^{-1}$). DFOM images of Cu–Zn$_x$ (D) and Cu (E) NW films after $\text{H}_2\text{O}_2$ treatment for 15 min. Camera photos of Cu–Zn$_x$ and Cu NW films before (F) and after (G) $\text{H}_2\text{O}_2$ treatment for 15 min.

After $\text{H}_2\text{O}_2$ treatment, the DFOM image of NW films in Figure 36D shows that the color of Cu–Zn$_x$ NWs changes from neutral gray to a Cu NW-like reddish-orange. This is due to the conversion of Zn to a transparent shell consisting of a mixture of ZnO and Zn(OH)$_2$ (see XPS below). In contrast, the color of Cu NWs in Figure 36E changes from reddish-orange to gray-black due to the oxidation of Cu to CuO, although the oxidized regions of Cu NWs are hardly visible due to the lack of light scattering. The changes in color after $\text{H}_2\text{O}_2$ treatment can also be observed in the camera photos in Figure 36F,G.
Unlike films of Cu NWs, the sheet resistance of films of Cu–Zn$_x$ NWs remains low after extended exposure to conditions designed to accelerate the oxidation of Cu. As shown in Figure 37A, the sheet resistance of Cu NWs increased dramatically in a dry oven at 160 °C and becomes insulating (>106 Ω sq$^{-1}$) after 12 h. This sheet resistance increase is accompanied by a decrease in the transmittance due to the conversion of Cu NWs to CuO, which has a larger absorption cross section.$^{123}$ In contrast, the sheet resistance of Cu–Zn$_x$ NW films increased less than 15% after 18 h, while the transmittance at $\lambda = 550$ nm increased from 76 to 83.6%. Both Cu and Cu–Zn$_x$ NWs exhibit similar changes in color after heating at 160 °C as with the H$_2$O$_2$ treatment (Figure 38).

![Figure 37.](image)

**Figure 37.** (A) Plots of sheet resistance of Cu–Zn$_x$ and Cu NWs vs time in a dry oven at 160 °C. (B) Plots of sheet resistance of Cu–Zn$_x$ and Cu NWs vs time at 85 °C/85% RH.
As shown in Figure 37B, similar results were obtained when the films were tested in a humidity chamber at 85 °C with a relative humidity of 85% (85 °C/85% RH). The sheet resistance of Cu NWs increased more rapidly under humid conditions, even given the lower temperature, becoming insulating in less than 30 min. The increase in sheet resistance is much slower for Cu–Zn₆ NWs; the sheet resistance increased from 25 to ∼300 Ω sq⁻¹ in 24 h. The transmittance of the Cu–Zn₆ NWs increases by 7% over the test period and is accompanied by a color change from gray to reddish-orange (Figure 39).
We performed X-ray photoelectron spectroscopy (XPS) on both Cu and Cu–Zn\textsubscript{s} NWs to further characterize their compositional changes after exposure to H\textsubscript{2}O\textsubscript{2}, elevated temperatures, and humidity. XPS of Cu NWs in Figure 40A exhibits peaks at 932.4 and 952.2 eV, characteristic of the 2p\textsubscript{3/2} and 2p\textsubscript{1/2} binding energies of Cu(0) metal.\textsuperscript{124} After exposure to H\textsubscript{2}O\textsubscript{2}, elevated temperatures, or humidity, the 2p peaks shift toward higher binding energy and additional rounded peaks from CuO appeared at 943.6 and 962.4 eV.\textsuperscript{124}
Figure 40. (A) XPS spectra of Cu species present on Cu NWs. (B) XPS spectra of Cu species present on Cu–Znₕ NWs. (C) XPS spectra of Zn species present on Cu–Znₕ NWs. (D) Auger spectra of Zn species (L₃M₄M₅ peak) present on Cu–Znₕ NWs. The Cu and Cu–Znₕ NWs were exposed to a 2 wt % solution of H₂O₂ in H₂O for 15 min, a dry oven at 160 °C for 18 h, or at 85 °C/85% RH for 24 h.

Figure 40B shows that after coating Cu NWs with a layer of Zn, the signals for Cu(0) decrease by approximately 8 times. After H₂O₂ treatment, heat, or humidity tests, these Cu(0) signals are nearly unchanged with no observable development of CuO signals, consistent with the fact that Cu NWs are protected from oxidation by the Zn layer.

Figure 40C shows XPS spectra for the 2p₃/₂ and 2p₁/₂ signals of Zn(0) and Zn(II) from Cu–Znₕ NWs before and after exposure to H₂O₂, elevated temperatures, and
humidity. There is a small shift of the peaks toward higher binding energies after the various exposures to oxidizing conditions, qualitatively consistent with the conversion of Zn(0) to Zn(II) species given the small spectral difference between Zn(0) and Zn(II).\cite{124, 125} In order to see the change in composition more clearly, we show Auger spectra in Figure 40D. Cu – Zn s NWs exhibit both a small Zn(0) peak at 993.4 eV and a broad Zn(II) peak centered at 988.6 eV, the latter consistent with the surface oxidation of Zn. After exposure to H2O2, heat, or humidity, the peak related to Zn(0) disappeared but different Zn(II) species appeared depending on the oxidation conditions. Exposure to H2O2 results in two peaks, one due to Zn(OH)2 and the other due to ZnO.\cite{124} After being heated at 160 °C for 18 h, ZnO is the dominant species on the surface of the nanowires. After testing at 85 °C/85% RH for 24 h, both the Zn(OH)2 and ZnO peaks have similar intensities. The reaction of Zn and ZnO with water to create Zn(OH)2 under humid conditions may explain the greater susceptibility of the Cu – Zn s NW film to oxidize and increase in resistance during exposure to H2O2 and 85% RH compared to the dry oven at 160 °C.

Sn can also be electroplated onto the Cu NWs and then oxidized to create a transparent shell that protects the Cu NWs from oxidation. Initial Sn plating attempts were conducted by holding the film at potentials more negative than −0.65 V in a 0.2 M deaerated phosphate buffer (pH 7.0) containing 1 mM SnCl2. However, constant-potential electroplating results in a rough coating consisting of nanoparticles with diameters in the tens to hundreds of nanometers (Figure 41, for example). It seems that
constant-potential electroplating causes Sn to deposit preferentially at certain surface sites. To overcome this problem, we alternated between reduction and oxidation of Sn on the surface of the Cu NWs with successive CV scans. Figure 42A shows successive CVs of a Cu NW film (32 Ω sq⁻¹, 85% at λ = 550 nm) under the same solution conditions. The electroplating of Sn(II) to Sn(0) on the nanowires is indicated by the increase in the current from the redox process of \( \text{Sn}^{II} + 2e^- \rightleftharpoons \text{Sn}^0 \) between −0.20 and −0.70 V. Figure 42B shows the Sn content of the Cu–Sn core–shell (Cu–Snₙ) NWs as a function of scan cycles, and Figure 42C shows that both the transmittance and the sheet resistance of the NW network decreased with increasing Sn content. The Cu–Snₙ NW network produced by 250 successive CV scans contained 15 mol % of Sn and exhibited a transmittance of 81.5% at λ = 550 nm and a sheet resistance of 25 Ω sq⁻¹.

**Figure 41.** DFOM (A), SEM (B), and TEM (C) images of Cu–Snₙ NWs formed by constant-potential electroplating at −0.65 V for 20 min.
Figure 42. (A) CVs (250 CV scan cycles, scan rate = 100 mV/s) of a Cu NW network in 0.2 M deaerated phosphate buffer (pH 7.0) with and without 1 mM SnCl₂ added to the solution. (B) Sn content of the film as a function of CV scan cycles. (C) Plots of sheet resistance and transmittance at λ = 550 nm vs scan cycles. (D) DFOM, (E) SEM, (F) TEM, and (G) EDS mapping images of Cu–Sn₅ NWs after 250 CV scan cycles.

Figure 42D–F shows DFOM, SEM, and TEM images of Cu–Sn₅ NWs. Similar to that of Cu–Zn₅ NWs, the electroplating of Sn occurred only on the surface of the Cu NWs, with no Sn deposited on the open areas of the substrate, and the color of light scattered from the NWs changes from reddish-orange to neutral gray upon coating with Sn. EDS mapping in Figure 42G shows that the Cu NW is largely coated with a thin layer of Sn. The average thickness of the shell was determined to be 3–5 nm after electrodeposition of ~15 mol% of Sn. Comparison of the images in Figure 42 with those in Figure 41 shows that coating Sn with successive reduction and oxidation scans results in a much smoother coating than constant reduction.
Figure 43A shows that coating as little as 5.2 mol % of Sn (100 CV scan cycles) can greatly reduce the oxidation of Cu NWs in a humid environment at 85 °C/85% RH. The resistance to oxidation increases with increasing Sn content up to ∼15 mol % of Sn (250 CV scan cycles), at which point the sheet resistance of the Cu–Sn NW film increases by only 105 Ω sq⁻¹ (from 25 to ∼130 Ω sq⁻¹) after 24 h. The XPS spectra in Supporting Information Figure 44A show that Cu(0) 2p₁/₂ and 2p₃/₂ peaks decrease by approximately 6 times after Sn coating and are retained after the humidity test, whereas 44B shows that the Sn(0) 3d₃/₂ and 3d₅/₂ peaks completely disappear after the humidity test, consistent with the conversion of Sn(0) to SnO₂ and/or Sn(OH)₄. The oxidation of Sn during the humidity test results in an increase in the transmittance of the Cu–Sn NW film from 81.5 to 83.8%. The full transmittance spectra of Cu NWs, Cu–Sn NWs, and Cu–Sn NWs after 24 h at 85 °C/85% RH in Figure 43B show that oxidation of the Sn shell allows the films to recover a significant portion of the transmittance loss after the initial Sn coating.

Figure 43. (A) Plots of sheet resistance ($R_s$) of Cu–Sn NWs of different Sn contents vs time at 85 °C/85% RH. (B) Plots of transmittance vs wavelength for Cu NWs, Cu–Sn NWs, and Cu–Sn NWs after humidity test.
NWs (15 mol % of Sn), and Cu–Sn NWs (15 mol % of Sn) after exposure to 85 °C/85% RH for 24 h.

**Figure 44.** XPS spectra of Cu (A) and Sn (B) species present on Cu NWs, Cu–Sn NWs and Cu–Sn NWs after humidity test at 85 °C/85% RH for 24 hrs.

A similar strategy of electroplating followed by oxidation can also be applied to In to create transparent shells that protect the Cu NWs from oxidation. A Cu NW network (32 Ω sq⁻¹, 85% at λ = 550 nm) was coated with In by electroplating In(III) (1 mM InCl₃) onto the Cu NW networks in an aqueous solution of 0.2 M NaCl. The CV in Figure 45A shows a redox couple corresponding to In⁺³ + 3e⁻ ⇄ In⁰. Continuous electroplating was conducted by holding the potential at −0.75 V vs NHE for 12 min, resulting in a Cu–In NW network with a transmittance of 78% at λ = 550 nm and a sheet resistance of 26 Ω sq⁻¹. The corresponding DFOM and SEM images are shown in Figure 45B,C. Plots of the sheet resistance of the films versus time at 85 °C/85% RH show that this Cu–In NW film is also highly resistant to oxidation (Figure 46); the sheet resistance of the film increased by only 64 Ω sq⁻¹ (from 26 to ∼90 Ω sq⁻¹) in 24 h.
Meanwhile, the transmittance increased from 78 to 83% due to the conversion of In to a transparent layer of In oxide (Figure 47).

**Figure 45.** (A) CVs of a Cu NW network in 0.2 M NaCl with and without 1 mM InCl$_3$ added to the solution. Scan rate, 100 mV/s. (B) DFOM and (C) SEM images of Cu-In NWs formed by electroplating at −0.75 V vs. NHE for 12 min.

**Figure 46.** Plots of sheet resistance of Cu and Cu-In NWs formed by electroplating at −0.75 V vs. NHE for 6 and 12 min vs. time of humidity test at 85 °C/85% R.H.
4.3 Benzotriazole as an Oxidation Resistant Shell for Copper Nanowire Transparent Conductors

The previous sections have explored metal and metal oxide options of protecting copper from oxidation. However, we also made an effort to use an organic species to prevent Cu NW corrosion. Benzotriazole (BTAH, Figure 48) is commonly used in industrial settings to protect bulk copper during polishing processes and against corrosion most likely due to the lone pair of electrons on nitrogen binding to metallic copper.\textsuperscript{126-127} Here we modified the experimental procedure of Susman et. al.\textsuperscript{128} to coat Cu NWs with BTAH.

![Benzotriazole](image)

Figure 48. Benzotriazole.

Cu NWs (dimensions $\sim L = 25 \mu m$, $D = 65$ nm) were coated onto glass slides via a Meyer rod and made conductive using a glacial acetic acid treatment and mechanical
pressing method. Once conductive, the slides were immersed in a 1% by weight aqueous solution of BTAH for various amounts of time. The slides were then rinsed with DI water and dried under N\textsubscript{2}. As indicated in Table 7, the optoelectronic properties of the nanowire films are negligibly affected by the addition of BTAH to the surface of the nanowires. The slight decrease in transmittance could be due to a slight residue that remains on the slides after the washing and drying step and the small increase in sheet resistance may be caused by BTAH molecules binding in between Cu NWs that were not fully pressed together thus creating an insulating contact. To study the resistance of these Cu NW/BTAH films toward oxidation, the samples were placed in a humidity chamber at 85 °C/85 RH and the change in sheet resistance over time was measured (Figure 49). Clearly, as the time the Cu NWs are immersed the BTAH solution increases, so does their resistance to oxidation with the 8 h and 24 h samples remaining conductive after 24 hours. Finally, OPVs were constructed in an identical manner to the CuNi OPVs discussed above (Figure 50). As in the above section detailing the CuNi OPV device, \(J_{sc}\) and \(V_{oc}\) for the Cu NW/BTAH OPVs (Table 8) were probably lower than the ITO based devices due to the lower transmittance of the Cu NW films themselves resulting in less current generation and poor PEDOT:PSS coverage resulting in shorts, respectively. These combine to result in a lower overall efficiency than the ITO based devises but one that is comparable to the CuNi and Ag NW devices fabricated above suggesting that an organic species could also be used to protect Cu NWs in functional devices.
### Table 7. Optoelectronic properties of Cu NW films before and after BTAH treatment

<table>
<thead>
<tr>
<th>Time in 1% BTAH</th>
<th>Before BTAH</th>
<th>After BTAH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%T (1%)</td>
<td>Rs (Ω sq⁻¹)</td>
</tr>
<tr>
<td>1 min</td>
<td>86.6</td>
<td>41</td>
</tr>
<tr>
<td>3 h</td>
<td>86</td>
<td>38</td>
</tr>
<tr>
<td>8 h</td>
<td>83</td>
<td>30</td>
</tr>
<tr>
<td>24 h</td>
<td>90.5</td>
<td>53</td>
</tr>
</tbody>
</table>

**Figure 49.** Sheet resistance change of Cu NW/BTAH films over 24 hours at 85 °C/85 RH.
Figure 50. Characteristic J-V curves of solar cells with ITO and Cu NWs/BTAH as the transparent electrode.

Table 8. Photovoltaic performance of the FTAZ BHJ solar cells. Film and Device Characteristics (λ = 550 nm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>%T</th>
<th>Rs (ohm/sq)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/BTAH</td>
<td>80</td>
<td>49</td>
<td>10.58</td>
<td>0.720</td>
<td>63.6</td>
<td>4.85</td>
</tr>
<tr>
<td>ITO Reference</td>
<td>88</td>
<td>20</td>
<td>11.20</td>
<td>0.831</td>
<td>75.0</td>
<td>6.98</td>
</tr>
</tbody>
</table>
4.4 Synthesis of Cu-Ag, Cu-Au, and Cu-Pt Core-Shell Nanowires and Their Use in Transparent Conducting Films

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 post-processing. Nanoscale deposition of less active metals onto more active metals, such as gold onto silver\textsuperscript{130-131} or silver onto copper,\textsuperscript{132-133} typically proceeds through galvanic replacement, which corrodes and oxidizes the metal template.\textsuperscript{134-135} Yang et. al.\textsuperscript{131} 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 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.
Figures 51A-C summarize the process of fabricating Cu NW networks from solution without silver. The dispersed Cu NWs (Figure 51A) are transferred to a nitrocellulose based ink and deposited onto a glass substrate via a Meyer rod (Figure 51B) resulting in a randomly dispersed network of NWs that is not conductive. If 0.39 mM AgNO₃ is added to a stirring Cu NW storage solution with 0.58 M ascorbic acid and 1 % of poly(vinylpyrrolidone) (PVP) (to hinder nanowire aggregation), the nanowires are evenly coated with silver. After this silver coating, the color of the nanowires becomes more grey (Figure 51D). The Cu-Ag NWs can then be purified and made into transparent films in the same manner as Cu NWs (Figure 51E) but are conductive as printed with a sheet resistance of 31 Ω sq⁻¹ at 79 %T. This performance can be further improved to 29 Ω sq⁻¹ at 84 %T with a brief rinse in acetone and water to remove any remaining nitrocellulose and PVP (Figure 51F). 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 nanowires. 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 mild heating step (at ≥120 °C) is usually required to remove any organics and anneal the NWs after coating.³³, ⁷¹
Figure 51. (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) Dark-field optical microscopy (DFOM) image of a Cu NW network at 85 %T. (D) A solution of Cu-Ag NWs after 0.39 mM AgNO₃ was added to the solution in (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.

Figures 52A & 52B show SEM images of the Cu NWs before and after coating with silver. The diameter of the nanowire increased by 13 nm after coating and, although the surface of the nanowire appears to be slightly rougher, there are no indications that the nanowire is galvanically etched by Ag⁺ ions in the presence of ascorbic acid. Figure 52C shows an SEM image of the Cu-Au NWs produced when AgNO₃ was replaced with HAuCl₄, keeping all the other reaction conditions constant.
Again, the average diameter of the nanowires increased by 14 nm and there is no evidence of etching. The TEM-EDS images in Figure 52D & 52E further show that the nanowires consist of a principally copper core with shells made of either silver or gold, respectively. Figure 53 shows that platinum can also be coated on the NWs with similar results.

**Figure 52.** 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, F) TEM-EDS images of Cu-Ag and Cu-Au NWs.
Figure 53. SEM image of Cu-Pt core-shell NWs. Average diameter was calculated from 50 distinct nanowires.

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 54A). 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. 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 Ω 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.\(^{80,81, 137}\) Indeed, films of Cu NWs washed with acetic acid instead of ascorbic acid resulted in comparable optoelectronic properties of 30
Ω 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 AgNO₃ in water. Figure 54B 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 HAuCl₄ and 0.005 M K₂PtCl₆ in water, again resulting in the expected nanotubes (Figures 54C and 55, respectively). If instead the Cu NW film was immersed in a solution containing 0.58 M ascorbic acid and 0.025 M AgNO₃ 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 54D). 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.

Figure 55. Cu-Pt nanotubes, made by immersing a Cu NW film in 5 mM K₂PtCl₆ after washing the Cu NWs with 0.58 M ascorbic acid.
To further investigate the role of ascorbic acid in preventing galvanic replacement, cyclic voltammograms (CVs) 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 56, 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 and/or copper ions. After addition of as little as 6 mM ascorbic acid (red curve), the oxidation and re-reduction 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. 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 M 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.\textsuperscript{138}
Finally we discuss the effect of the silver shell thickness on the optoelectronic properties and oxidation resistance of Cu-Ag NW films. Figure 57A shows plots of transmittance (at a wavelength of 550 nm) vs. 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.\textsuperscript{84} 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 58). 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 59 and 60 respectively) than Cu NWs, likely due to the relatively higher resistivity of gold ($\rho = 2.21 \times 10^{-8} \Omega\text{ m}$) and platinum ($\rho = 10.5 \times 10^{-8} \Omega\text{ m}$) compared to copper ($\rho = 1.7 \times 10^{-8} \Omega\text{ m}$).
A

T (%) vs. $R_s$ ($\Omega \text{ sq}^{-1}$)

- ITO
- Cu NWs $L/D = 360$
- Ag NWs $L/D = 300$
- Cu-Ag NWs $L/D = 320$
- Cu-Ag NWs $L/D = 260$

B

$R$ ($\Omega \text{ sq}^{-1}$) vs. Time at 160 °C (hrs)

- Cu NWs
- Ag NWs
- Cu-Ag NWs (5 nm Ag)
- Cu-Ag NWs (15 nm Ag)

C

$R$ ($\Omega \text{ sq}^{-1}$) vs. Time at 85 °C/85% RH (hrs)

- Cu NWs
- Ag NWs
- Cu-Ag NWs (5 nm Ag)
- Cu-Ag NWs (15 nm Ag)
Figure 57. (A) Plots of transmittance vs sheet resistance for Cu NWs, Ag NWs, and Cu-Ag NWs with different aspect ratios ($L/D$). Plots of sheet resistance vs time for Cu NWs, Ag NWs, and Cu-Ag NWs in (B) a dry oven at 160 °C and (C) at 85°C/ 85% RH.

![Figure 57](image1.png)

Figure 58. Transmittance spectra of Cu NWs ($R_s \sim 45 \, \Omega \, \text{sq}^{-1}$), Cu-Ag NWs with 5 nm and 15 nm shell thicknesses ($R_s \sim 45 \, \Omega \, \text{sq}^{-1}$), Cu-Au NWs ($R_s \sim 250 \, \Omega \, \text{sq}^{-1}$), and Cu-Pt NWs ($R_s \sim 4500 \, \Omega \, \text{sq}^{-1}$).

![Figure 58](image2.png)

Figure 59. (A) Camera images showing the transition from Cu to Cu-Au NWs after the addition of 0.075 mL of HAuCl$_4$ (0.025 M) (AA=ascorbic acid). (B) DFOM image showing a network of Cu-Au NWs after the addition of 0.075 mL of HAuCl$_4$.

![Figure 59](image3.png)
Figure 60. DFOM image showing a network of Cu-Pt NWs after the addition of 0.947 mL of 0.005 M K₂PtCl₆ to a solution of Cu NWs/PVP/DEHA and ascorbic acid (0.58 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 °C, the sheet resistance of the Cu NW films increased from 39 Ω sq⁻¹ to 80 Ω sq⁻¹ in only 30 minutes due to thermal oxidation (Figure 57B). The Cu-Ag NW samples of \( L/D = 320 \) and 260 remained conductive for at least 24 hours, 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 °C.

When subjected to a humid environment (85% RH) at 85 °C, the sheet resistance of Cu NW films increases by orders of magnitude in a few hours (Figure 57C), 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 ~2 orders of magnitude over 24 hours, 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 hours.
5. Summary and Future Directions

The use of nanowires in printed electronics, specifically Cu NWs in transparent conductors, should become more common following this work. I have shown that nanowires provide the least amount of contacts in conductive thick films and thus provide the lowest resistivity, compared to nanoparticles and microflakes, when deposited at low temperature. I have also shown that Cu NWs have the potential to replace ITO in transparent conductors as long as the aspect ratio of the nanowires is controlled to minimize nanowire-nanowire contact. From the above work, there now exists a completely room-temperature, solution phase method to render Cu NWs conductive without the use of high temperature H$_2$ annealing. Finally, I also discussed several methods of protecting Cu NWs from oxidation while maintaining excellent optoelectronic properties. Most notably the ability to electrolessly plate a thin layer of silver onto copper without galvanic etching provides Cu NWs the same optoelectronic properties as Ag NWs at the same aspect ratio. This should spur future efforts into plating silver onto high aspect ratio Cu NWs in order to match the performance of pure Ag NWs at a sheet resistance and transmittance better than ITO. Future work involving the use of Cu-Ag nanomaterials in thick film printed electronics as well as conductive filaments and composites should also help reduce the cost of printed electronics as one can match the performance of silver-based materials at a lower cost.
6. Experimental

6.1 The Effect of Morphology on the Electrical Resistivity of Silver Nanostructure Films

6.1.1. Synthesis of Various Silver Nanomorphologies

6.1.1.1. Short Nanowire Synthesis

Short Ag NWs (length = 6.2 ± 2.4 μm, diameter = 48 ± 10 nm) were synthesized according to the polyol method. First, 158.4 mL of ethylene glycol (EG) were added to a 500 mL round bottom flask which was subsequently stoppered and heated to 130 °C in an oil bath for 1 hour. Separately, the following solutions were prepared: (1) 0.257 g NaCl in 20 mL EG, (2) 0.081 g Fe(NO3)3 in 10 mL EG, (3) 1.05 g PVP (MW = 55,000) in 25 mL EG, and (4) 1.05 g AgNO3 in 25 mL 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 seconds between each addition. The flask was then stoppered and the reaction was allowed to stir at 250 rpm and 130 °C for 6 hours. Finally, the short Ag NWs were purified by washing twice with acetone and once with water and were stored in water.

6.1.1.2. Long Nanowire Synthesis

Long Ag NWs (L = 27 ± 12 μm, D = 150 ± 30 nm) were synthesized via the same polyol method described above except the solution of EG was preheated to 125 °C for one hour and left at this temperature for five minutes after the four solutions had been added. After these five minutes were over, the oil bath temperature was raised to 130 °C.
and the contents were left stirring at 150 rpm for six hours. The washing and storage procedure was also the same as for the short Ag NWs.

### 6.1.1.3. Silver Nanoparticle Synthesis

Ag NPs (average particle size = 27 ± 8 nm) were synthesized following the procedure by Magdassi et. al. In a 50 mL round bottom flask, 4.5 g AgC$_2$H$_3$O$_2$ (Aldrich), 2.9 g 20 % poly(acrylic acid) (diluted from 40 % poly(acrylic acid) MW = 8000; Aldrich), and 28 mL distilled water were combined and heated to 95 °C for 15 minutes while stirring. Next, 3.4 g of 30 wt % ascorbic acid (Aldrich) were added to the flask and the mixture was heated and stirred for 30 minutes. The Ag NPs were washed with and stored in distilled water.

### 6.1.1.4. Silver Microflake Synthesis

A scaled up version of the seeded synthesis by Audoit et. al. was used to synthesize Ag MFs (length = 1.6 ± 0.3 μm, thickness = 51 ± 8 nm). First, silver seeds were synthesized by mixing 24 mL sodium citrate dihydrate (0.2 mM, Aldrich), 0.06 mL AgNO$_3$ (0.025 M, Aldrich), 0.06 mL iced H$_2$O$_2$ (2.418 M, Acros Organics), and 0.08 mL distilled water followed by the dropwise addition of fresh, cold 0.8 mL NaBH$_4$ (0.05 M, Alfa Aesar) under vigorous stirring. The mixture was allowed to stir for an additional 3 minutes and the resulting yellow solution was collected without purification. These silver seeds (2 mL) were added to 8 mL of distilled water, 0.5 mL sodium citrate dihydrate, and 1 mL of ascorbic acid (0.1 M, Aldrich) while stirring. To synthesize silver
nanoplates, 0.3 mL AgNO$_3$ (0.01 M) were added to this mixture via syringe pump at a rate of 3.0 mL h$^{-1}$. The resulting blue solution of silver nanoplates was used in the next step without purification. To a 500 mL flask, 10 mL of silver nanoplates, 90 mL of distilled water, and 100 mL of ascorbic acid (0.008 M) and sodium citrate dihydrate (0.00267 M) were combined under moderate stirring. Then 100 mL of AgNO$_3$ (0.004 M) were injected into the flask via syringe pump at a rate of 55 mL h$^{-1}$. Once the addition of AgNO$_3$ was complete, 100 mL of the gray colored product were added to a clean round bottom flask (without purification) with 100 mL of ascorbic acid (0.008 M) and sodium citrate dihydrate (0.00267 M) while stirring. Again, 100 mL of AgNO$_3$ (0.004 M) were injected into this flask via syringe pump at a rate of 67 mL h$^{-1}$ while stirring. This process was completed once more with a AgNO$_3$ addition rate of 100 mL h$^{-1}$. Finally, 30 mL NaOH (0.5 M Acros Organics) were added to the microflakes and they were collected by washing three times with distilled water.

6.1.2. Film Fabrication and Annealing Experiments

Wells were constructed from 0.12 mm-thick double sided tape by using a 7 mm diameter hole punch and adhering the tape to glass slides. For both nanowire shapes and the nanoflakes, the glass slides were pretreated by sonicating in acetone then IPA; this was not necessary for the nanoparticles. The short nanowires, particles, and nanoflakes were concentrated to 20 mg mL$^{-1}$ and deposited from water into separate wells (0.05 mL of solution). These wells were then placed in a 70 °C to remove the water
and finally placed in a tube furnace at the desired temperature (200 – 400 °C). Since the long nanowires would aggregate at higher concentrations, 0.05 mL of 2 mg mL⁻¹ were deposited into the wells then dried at 70 °C. This was repeated for a total of 10 times in order for the mass of silver deposited to match the other morphologies (1 mg).

### 6.1.3. Instrumentation and Characterization

Dark field optical microscopy (DFOM) images were taken with an Olympus BX51 microscope. SEM (FEI XL30 SEM-FEG) images and XRD (Panalytical X’Pert PRO MRD HR XRD) spectra were taken at the Shared Materials Instrumentation Facility at Duke University. Metal concentration measurements were completed using a Perkin Elmer 3100 atomic absorption spectrophotometer (AAS). For all films sheet resistance values were measured using a four-point probe (Signatone SP4-50045TBS) and thicknesses were calculated from the mass of silver deposited.

### 6.2 Copper Nanowire Structure Property Relationship in the Context of Transparent Conductors

#### 6.2.1. Effects of Length Dispersity and Film Fabrication on the Sheet Resistance of Copper Nanowire Transparent Conductors

**6.2.1.1. Copper Nanowire Transparent Conductor Films**

Cu NWs with an average aspect ratio $L/D = 330$ were synthesized using the method described by Rathmell et al.\(^{51}\) with an average diameter of 76 nm. A modified method described by Ye et al.\(^{34}\) was used to synthesize Cu NWs with $L/D = 150$ and 570 and average diameters of 78 and 64 nm, respectively. Nanowire diameters were
measured using a FEI XL 30 SEM-FEG and ImageJ (http://imagej.nih.gov/ij/).
Measurements of nanowire lengths were made with an Olympus BX51 optical
microscope and the Olympus Stream Image Analysis software. The nanowires were
deposited as thin film networks by transferring nanowires dispersed in a nitrocellulose-
based ink onto PET using a Meyer rod. The films then received one or more post
treatments to remove oxidized layers, reducing the nanowire-nanowire contact
resistance, and thereby improving sheet resistance. Post treatments included repeated
rinsing in acetic acid, pressing at room temperature (80 bar, 1 minute), plasma
cleaning under a forming gas for 10 minutes, and annealing in a tube furnace under
hydrogen gas at 175 °C for 30 minutes. The films were then immediately vacuum
sealed and stored in a nitrogen-rich atmosphere until characterization. The average
sheet resistance of the Cu NW films determined from 5 measurements in a roughly 2.5
cm × 2.5 cm area with a four-point probe (Signatone S-1160A-5). The probe separation
distance for this instrument is 1 mm, significantly greater than the length of the
nanowires in each film. The specular transmittance was determined using UV/VIS/NIR
measurements (Cary 6000i). A calibration curve (Figure 61) for determining \( A_s \) was
constructed from transmittance measurements of Cu NWs deposited on PDMS via the
method described by Bergin et al.
Figure 61. Calibration curve for the determination of $A_F$ from transmittance measurements of Cu NW films on PET. A linear fit was obtained using OriginPro 8.1 with $y$ intercept = 97.41 and slope = -89.71

6.2.1.2. Measurement and Calculation of Area Fraction Using RBS

Rutherford backscattering spectrometry (RBS) data were collected at normal beam incidence using $^4$He$^+$ ions accelerated to $E_0 = 2.02$ MeV for each sample. The spot size of the incident beam was set to $\sim 20$–$30$ mm$^2$. A passivated implanted planar silicon (PIPS) detector with solid angle $\Omega = 1.59$ msr was placed at an angle $\theta = 170^\circ$ relative to the incident beam. The total collected charge for each sample was 10 $\mu$C. Thin films of copper metal were deposited using a thermal evaporator. These films are used as standards for the calculation of area coverage for the copper nanowire TCs. The copper
thin films used in this paper are 120–180 nm thick as determined by RBS and AFM measurements.

In RBS measurements, the amount of energy that a back-scattered ion loses in the inelastic collisions with the atoms in and on a sample surface depends on the type of incident ion used, the incident energy, the scattering atoms’ Z-number, depth within the sample, and the path that the ion takes through the sample before being collected by the detector.\textsuperscript{82-83} Several types of scattering events can occur between the incident ion and the atoms in a nanowire transparent conductor sample. If the ion scatters off of a copper atom at the surface of one of the nanowires it will lose the smallest amount of energy, corresponding to the front edge of the energy peak in the spectrum (Figure 11). The tailing of the copper peak to lower backscattering energy is due to scattering from a copper atom that is not on the surface of a wire or secondary collisions with copper atoms after interaction(s) with other atoms in the sample. These latter interactions are what necessitate the use of a copper metal thin film standard in order to calculate $A_F$. In RBS measurements, the total number of detected particles or yield, $Y_i$, from an element, $i$, in a sample is related to the atomic areal density of that element, $(Nt)_i$, by

$$Y_i = \sigma_{R(E, \theta)} \Omega Q (Nt)_i$$

(1)

where $\sigma_{R(E, \theta)}$ is the differential backscattering cross section of the element, $E$ is the incident beam energy, $\theta$ is the angle at which the detector is placed relative to the beam, $\Omega$ is the solid angle subtended by the detector, and $Q$ is the total number of
incident ions or dose. The atomic areal density and subsequently \( A_f \) can be determined for the nanowire samples by comparing results from Equation 1 for the nanowire transparent conductor and the copper thin film standard. Noting that \( \Omega \) and \( Q \) depend solely on the instrumental setup and, thus, are constant for our experiments, we can solve for the product \( \Omega \cdot Q \). Next, we solve for the atomic areal density of the element \( i \) in the nanowire sample, \((Nt)^{NW}_i\), and obtain an expression for calculating the atomic areal density of copper in the nanowire transparent conductor:

\[
(Nt)^{NW}_i = \frac{Y^{NW}_i}{Y^o_i} \frac{\sigma_R(\bar{E}, \theta)_i^o}{\sigma_R(\bar{E}, \theta)^{NW}_i} (Nt)^o_i
\]  

(2)

where the superscript “\(^o\)” denotes quantities from the copper thin film. All of the terms on the right can be obtained from either RBS data or from the instrumental setup except for the scattering cross sections which must be calculated. For a large \( \theta \) the scattering cross section, \( \sigma_s \), can be approximated by

\[
\sigma_R(\bar{E}, \theta) \simeq 0.02073 \left[ \frac{Z_1 Z_2}{4E} \right]^2 \left[ \sin^{-4} \left( \frac{\theta}{2} \right) - 2 \left( \frac{M_1}{M_2} \right)^2 \right]
\]  

(3)

where \( Z_1 \) and \( M_1 \) are the atomic number and mass for the incident particles, respectively, and \( Z_2 \) and \( M_2 \) are for the target atoms. For the nanowire samples we can simply use the incident energy, \( E_0 \), for the calculation of the scattering cross section since the vast majority of scattering events are close to the surface. For thin films, we need to account for additional energy losses that are dependent on the thickness of the calibration film. In the so-called surface energy approximation, SEA, we calculate the mean energy, \( \bar{E} \), to a
first approximation within the film and use this quantity when calculating the cross section

\[
\bar{E} = E_0 - \frac{\Delta E_{\text{in}}^{\text{SEA}}}{2}
\]  

(4)

where the energy loss is calculated from data by

\[
\Delta E_{\text{in}}^{\text{SEA}} = \varepsilon_i (E_0) (Nt)_i
\]  

(5)

The stopping cross section of the target element, \( \varepsilon_i \), is tabulated. We can now readily calculate \((Nt)_i^{NW}\) for each nanowire transparent conductor from RBS data. From this quantity \( A_F \) is calculated assuming that all nanowires can be modeled as cylinders with constant diameter \( D \) which is taken to be the experimentally obtained average diameter. The junctions where nanowires cross are double counted in our calculation. However, this additional contribution is negligible in the overall calculation of the area fraction for high aspect ratio wires near the percolation threshold. The number of atoms per unit volume is considered to be equivalent to the bulk atomic density of the material, \( \rho_B \).

The fraction of the surface area of a transparent conductor covered by nanowires, \( A_F \), is directly proportional to the atomic areal density and the dimensions, \( <L> \) and \( <D> \), and inversely proportional to the number of atoms per wire, \( n \), which is calculated using \( \rho_B \), the volume of a wire, and the molecular weight of the nanowire component element, \( M_i \).

\[
n = \frac{\pi \rho_B D^2 L}{4 M_i}
\]  

(6)
Substitution leads to the expression for calculating the area fraction from the atomic areal density measured by RBS for a nanowire transparent conductor:

$$A_F = \frac{4(Nt)_i^{NW} M_i}{\pi \rho_B D}$$  \hspace{1cm} (7)

### 6.2.1.3 Application of Length Disperity to Simulations

Our Monte Carlo method for pseudo-2D rod networks was previously described. In brief, a nanowire network deposited on a flat substrate is represented by a network of isotropically oriented, interpenetrating cylindrical rods confined to the $x$–$y$ plane of a supercell with dimensions $1 \times 1 \times D_{rod}$, where $D_{rod}$ is the diameter of an individual rod (typically $D_{rod} = 10^{-5}$ to $10^{-4}$ a.u.). The internal resistance of the rods is assumed to be zero while the resistance of the surrounding medium is infinite. Therefore all resistance in the network of rods is attributed to a single effective contact resistance, $R_c$, applied to each of the rod–rod intersections. This is understood to be the average contact resistance between nanowires in the transparent conductor.

Distributions of rod lengths to be used in the simulations were determined by fitting experimental measurements of nanowire lengths with a lognormal distribution (Figure 10). The fit routine followed the form

$$f(L) = A + \frac{B}{\sigma L \sqrt{2\pi}} e^{-\frac{\ln\left(\frac{L}{\xi}\right)^2}{2\sigma^2}}$$  \hspace{1cm} (8)
where the constants $A$ and $B$ are fitting parameters. The best fitting distribution with average length, $<L>$, and standard deviation, $\sigma$, was then applied to the rods in the simulation via the lognormal random number generator function from the GNU Scientific Library. To verify that the proper distributions were being produced, the lengths of the rods used in the simulation were fit using the same lognormal routine and compared with the parameters set in the simulation (Figure 62a).
Figure 62. (a) Distributions of rod lengths produced when applying the lognormal distribution in our simulations for the specific case of $A_F = 0.10$, $D = 0.0001$ a.u., $<L>/D = 500$, $\sim 17$ 000 rods per distribution. Three standard deviations for the lognormal are shown: 0.05, 0.25, and 0.50. As the standard deviation decreases, the distribution approaches that of the monodisperse case where all rods have $L = <L> = 0.05$ a.u. (b) Calculated sheet resistance versus area fraction for $D = 75$ nm corresponding to the three distributions shown in part (a).

The rods have constant $D$, constant $<L>/D$ and varying standard deviation to give varying degrees of dispersity. The sheet resistance of pseudo-2D rod networks made from rods with these length distributions decreases with increasing length dispersity (Figure 62b). For example, across the range of area fractions tested a high lognormal dispersity ($\sigma = 0.50$) decreases the sheet resistance by $\sim 50\%$ relative to a low level of dispersity ($\sigma = 0.05$). This result is consistent with longer rods being more effective in constructing a percolated network. Experimentally, typical Cu NWs have measured length dispersity of $\sim 0.20$, such that at a fixed areal coverage the reduction of the sheet resistance relative to monodisperse nanowires of the same average length is $\sim 20\%$. The critical area fraction for percolation, $A_c$, was extracted from the simulations via fitting the conductivity values from the simulations using the relationship

$$\sigma = s \left( \frac{A_F - A_C}{A_C} \right)^t$$

(9)

where $s$ is simply a scalar. Here we are fitting over $A_F = 0.01$–0.60 which yields higher than universal values for the percolation exponent, $t$, which varied from 1.8 to 2.139 In Figure 63 we show the values for $A_c$ extracted from simulations at three $<L>/D$ with
varying levels of polydispersity. As expected, $A_C$ decreases significantly as a function of the aspect ratio, $<L>/D$.\textsuperscript{139} However, $A_C$ has a weak dependence on the length polydispersity related to the increase in the weighted average length, $<L>_w$, with $\sigma$, as was found by others previously.\textsuperscript{140-143} The critical area fraction of a polydisperse system, $A_{C\_poly}$, is given by

$$A_{C\_poly} = \frac{3.7}{\left(2 + \frac{8}{\pi^2}\right) + \left(\frac{<L>_w + D}{D} - \frac{2}{<L>}\right)}$$  \hspace{1cm} (10)$$

Here we hold the excluded volume to the value of 3.7 and $D$ is constant.\textsuperscript{4} At high aspect ratios this relationship is dominated by the weight average term. In the mean field approximation the system is monodisperse when $<L>_w/<L> = 1$ (solid line in Figure 63). As the system becomes more polydisperse this ratio increases and thereby decreases the percolation threshold for a given $<L>/D$; Figure 63 shows the results from eqn (10) for $<L>_w/<L> = 1.5$ (long dashes) and 2 (short dashes). In comparison, the simulations exhibit a distinct lack of sensitivity to the level of dispersity across this range of $<L>/D$. This is comparable with previous findings for simulations of 3D rod networks that $A_C$ is insensitive to polydispersity for narrow Gaussian distributions where the standard deviation is <30%.\textsuperscript{144} It is interesting that as the aspect ratio increases, the further the simulated data deviates from monodisperse behavior. This again highlights the significant impact of longer rods on percolation.
Figure 63. The percolation threshold, $A_C$, of simulations of networks of rods with varying levels of polydispersity according to lognormal distributions is presented (points). The calculated curves for the percolation threshold of polydisperse networks according to eqn (10) are compared to the values from simulation. The solid line represents the monodisperse case with $<L >/<L>=1$ along with polydisperse cases $<L >/<L>=1.5$ (long dashes) and $<L >/<L>=2$ (short dashes).

6.2.2. A Rapid Synthesis of high Aspect Ratio Copper Nanowires for High-Performance Transparent Conducting Films$^{34}$

6.2.2.1. Synthesis of Copper Nanowires

In a typical copper nanowire synthesis, NaOH (15 M, 20 mL), Cu(NO$_3$)$_2$ (0.1 M, 1 mL) and EDA (1.5 - 4.5 mmol) were mixed at an elevated temperature (60 - 70 °C) for 3 minutes under stirring at 700 rpm. N$_2$H$_4$ (35 wt %, 0.12 - 0.22 mmol) was then added to the solution and the stirring was stopped after two minutes. The solution color changed from deep blue to clear and colorless to dark red, indicating the formation of thin Cu
NWs. In the case of excessive N$_2$H$_4$ (e.g. N$_2$H$_4$ = 10.5 mM), the layer of the copper nanowires at the air-water interface turned pink 19 min after addition of N$_2$H$_4$. Otherwise, the Cu NWs floated to the air-water interface ~30 min after addition of N$_2$H$_4$ and remained dark red. The Cu NWs were extracted from the reaction solution by adding ~15 mL of an aqueous solution consisting of 3 wt % polyvinylpyrrolidone (PVP, MW 10,000) and 5 wt % diethylhydroxylamine (DEHA). After vigorously shaking and swirling this suspension, a layer containing the Cu NWs accumulated at the top of the suspension, and this layer was removed from the reaction solution with a separation funnel. The Cu NWs were further washed with a solution of 3 % PVP and 5% DEHA for three cycles of centrifugation (10 min at 2000 rpm) and decantation. To determine the yield of Cu NWs, the Cu NWs were dissolved in HNO$_3$, and the resulting solution was analyzed with an atomic absorption spectrometer (AAS, Perkin Elmer 3100).

6.2.2.2. In Situ Growth of Copper Nanowires

A mixture of NaOH (15 M, 20 mL), Cu(NO$_3$)$_2$ (0.1 M, 1 mL), EDA (2 and 4.5 mmol) and N$_2$H$_4$ (35 wt %, 0.42 mmol) was stirred at room temperature. The solution turned clear and colorless after 10 minutes and was used as the growth solution. Small aliquots (~6.5 μL) of the as-prepared growth solution were transferred to the cell made of two 22 mm × 22 mm coverslips (VWR, 0.17 mm thickness) spaced by a 120-μm-deep double sided adhesive well (Invitrogen, Secure-SealTM spacer, 9 mm diameter). The solution in the cell was then heated to the desired temperature (70 °C) on a transparent
heater, and the growth of the nanowires was visualized and recorded through an optical microscope (Olympus BX51) fitted with a SC30 CMOS camera. Time-lapsed images focused at the interface of the growth solution and the bottom coverslip were taken at a frame rate of 1 frame per second (fps) using the Olympus Stream imaging software. The lengths of each nanowire at different time points were measured with ImageJ.

6.2.2.3. Preparation of Transparent Conducting Films

Transparent conducting films of Cu NWs were made in a manner similar to previous work. The Cu NWs were transferred from the storage solution (3% PVP and 5% DEHA) into a 1.5 mL centrifuge tube after the initial washing steps. This suspension was centrifuged at 2000 rpm for 1 min. The Cu NWs were washed 3 times using a solution of 3% DEHA to ensure PVP was removed. After the PVP was removed, the Cu NWs were washed with ethanol to remove the majority of the water and then washed once more with the nitrocellulose based ink formulation. The Cu NWs were re-dispersed in the ink by vortexing to form a homogeneous suspension. To prepare a transparent nanowire electrode, glass microscope slides were placed onto a clipboard to hold them down while the nanowire ink (50 μL) was pipetted in a line at the top of the slide. A Meyer rod (Gardco, 51.3 μm wet film thickness) was then quickly (< 1 second) pulled down over the nanowire ink by hand, spreading it across the glass into a thin, uniform film. Different densities of nanowires on the surface of the substrate were obtained by varying the concentration of the nanowires in the ink. The film was dry after
approximately 60 seconds. To remove organic material from the nanowire network, the films were cleaned in a plasma cleaner (Harrick Plasma PDC-001) for 10 minutes in an atmosphere of 95% N\textsubscript{2} and 5% H\textsubscript{2} at a pressure of 600-700 mTorr. The nanowire films were then heated at 225 °C in a tube furnace for 30 minutes under a constant flow of H\textsubscript{2} (350 mL min\textsuperscript{-1}) to anneal the wires together and decrease the sheet resistance. The transmittance and sheet resistance of each nanowire film was measured using a UV-Vis-NIR spectrophotometer (Cary 6000i) and a four-point probe (Signatone SP4-50045TBS). Each data point in Figure 25 is the average of 5 measurements.

6.3 Methods of Rendering Copper Nanowires Oxidation Resistant and Their Subsequent Application in Electronic Devices

6.3.1. Solution-Processed Copper-Nickel Nanowire Anodes for Organic Solar Cells

6.3.1.1. Materials and Instrumentation

For all nanowire 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 Figures 1D, 2D, and 4A are each an average of 5 probe measurements. Metal concentration measurements were completed using a Perkin Elmer 3100 atomic absorption spectrophotometer (AAS). Pressing was performed with a shop press (model H6233Z) from Grizzly Industrial. Plasma cleaning was performed with a Harrick Plasma PDC-001. Optical microscopy images were taken with an Olympus BX51 microscope. SEM
(FEI XL30 SEM-FEG), TEM (FEI Tecnai G² Twin), and AFM (Digital Instruments Dimension 3100) images were taken at the Shared Materials Instrumentation Facility at Duke University. Humidity chamber measurements were made in a Test Equity 200H Series Temperature/Humidity Chamber at 85 °C/85 RH. Photovoltaic performance was characterized with a solar simulator (Oriel 91160, 300 W) under AM1.5 global one sun (100 mW/cm² calibrated by a NREL certified standard silicon cell) at room temperature in a glove box. Current density vs. potential (J-V) curves were recorded with a Keithley 2400 digital source meter. The incident photon-to-current conversion efficiency (IPCE) measurements were carried out under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode.

### 6.3.1.2. Preparation of Nanowire Films

Copper nanowires (L = 20 ± 5 μm, D = 67 ± 15 nm) were synthesized by previously reported methods and donated by NanoForge Corp. To separate the nanowires (1.4 mg mL⁻¹ copper) from their storage solution of polyvinylpyrrolidone (PVP, 1 wt % in DI water, Aldrich) and diethylhydroxylamine (DEHA, 1 wt % in DI water, Aldrich), several purification steps were required. First, an aliquot (1 mL) of nanowires was collected and centrifuged at 2000 rpm for 5 minutes followed by decantation of the PVP/DEHA supernatant. The nanowire aggregates were then washed three times with DEHA (1 mL, 3 wt % in DI water) to remove the remaining PVP. Next,
the nanowires were washed with 190 proof ethanol (1 mL, Koptec) to extract any residual water. The nanowires were then washed with an ink formulation consisting of 0.06 g nitrocellulose (Scientific Polymer) dissolved in 2.94 g acetone (EMD) with subsequent addition of 3 g ethanol (Pharmaco-Aaper), 0.5 g ethyl acetate (Aldrich), 1 g pentyl acetate (Aldrich), 1 g isopropanol (BDH), and 1.7 g toluene (Aldrich). The suspension was briefly vortexed and sonicated (<5 seconds) between washing steps.

Prior to preparing the Cu NW transparent electrodes, the glass substrates (3 in × 1 in microscope slides, VWR) were sonicated in acetone for ten minutes and transferred to isopropanol to remove surface contaminants. The slides were wiped dry with a kimwipe and blown dry under air immediately prior to nanowire deposition. Following decantation of the ink wash supernatant, a small amount (0.3 mL) of the ink was added to the nanowires resulting in a final Cu NW concentration of ~4.5 mg mL⁻¹. This suspension was vortexed to disperse the nanowires 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 second) drawn down the slide by hand to evenly spread the nanowire coating. The amount of ink added to the nanowires can be adjusted to vary the Cu NW concentration, and thus the transmittance and conductivity of the resulting film.

The slides coated with Cu NWs were dried in air for 10 minutes at 80 °C. Once the slides returned to room temperature, they were dipped in glacial acetic acid (Aldrich) for 2 seconds (Figure 1A), dried under N₂ gas, and placed in an 80 °C oven for
45 seconds. Following four cycles of this procedure, the slides were allowed to cool to room temperature and then dipped in acetic acid and dried under N₂ twice more without additional oven drying. In some cases the slides were pressed at 80 bar at room temperature for one minute between glass slides functionalized with 1H, 1H, 2H, 2H – perfluoroctyltriethoxysilane (Aldrich). To perform this functionalization, the slides were first plasma cleaned in air at a pressure of 0.8 to 0.93 mbar for 1 minute and placed in a dessicator under vacuum overnight along with an open vial containing 1 drop of 1H, 1H, 2H, 2H– perfluoroctyltriethoxysilane.

For the Cu NW films annealed under H₂, the films were coated from the ink and dried in the oven as above. Instead of an acetic acid dip, the films were plasma cleaned under forming gas (95% N₂, 5% H₂) for 10 minutes at a pressure of 600 to 700 mTorr to remove residual organic material from the electrodes. Next, the electrodes were heated to 175 °C in a tube furnace under constant H₂ flow (600 mL min⁻¹) for 30 minutes to eliminate the remaining nitrocellulose and anneal the nanowires together.⁵¹

Silver nanowires were synthesized following previously published methods to give nanowires with dimensions of L = 15 ± 3 μm and D = 63 ± 7 nm.⁸⁴,¹⁴⁵ Electrodes of Ag NWs were prepared in the same manner as Cu NW electrodes. After centrifuging and decanting the water from the nanowires, two rinses of ethanol were performed to ensure water removal. The Ag NWs were washed with the ink formulation, dispersed in ink, and coated onto glass slides via a Meyer rod. In order to remove any remaining
organic material, the films were plasma cleaned under forming gas (95 % N₂, 5 % H₂) at a pressure of 600-700 mTorr for 10 minutes.

6.3.1.3 Electroless Nickel Plating

The nickel plating bath was prepared by heating 30 mL of DI water to 75 °C while stirring at 225 rpm. Ni(NO₃)₂ (0.1 M, 200 μL, Alfa Aesar) and hydrazine (35 % weight, 150 μL, Aldrich) were added to the DI water after it reached the desired temperature. The Cu NW electrodes were then dipped into a 0.8 mM Pd²⁺ activation solution (10 mg sodium tetrachloropalladate from Aldrich in 40 g 190 proof ethanol from Koptec) for 20 seconds and immediately transferred to the Ni plating solution for various plating times. The amount of Ni deposited on the Cu NWs was measured by dissolving the CuNi films in concentrated nitric acid, and measuring the ratio of Ni to Cu with an AAS. By plotting the ratio of nickel to copper in the nanowires versus time in the plating bath, the amount of Ni plated onto the Cu NWs could be estimated and controlled (Figure S1). To prepare samples for the humidity chamber, the conductive films were first cut into 2.54 cm × 1 cm glass slides and silver paste was applied in strips to outline a 1 cm × 1 cm square. Next, the samples were inserted into the humidity chamber and the silver paste was connected through the silicone port plug of the chamber to a multimeter.
6.3.1.4. Measurement of Pd Content and Cost.

Three Cu NW slides were treated with glacial acetic acid and pressed at 80 bar for 1 minute to a final transmittance of 91.5%. Each slide was then separately dipped into the Pd\textsuperscript{2+} activation solution described above for 20 seconds. The Pd-coated Cu NWs were then scraped off of the slides with a razor blade and collected in a vial. Aqua regia (0.5 mL) was added to dissolve the NWs and this solution was diluted to 12.5 mL with deionized water. The ratio of the mass of Cu to Pd was determined by AAS to be 10.2, and the cost of Pd was calculated to be $0.13 \text{ m}^{2}$ (Table 9, Appendix).

6.3.1.5. Fabrication of BHJ OPV Electrodes

For the reference device on ITO-coated glass (Thin Film Devices, Inc.), a pre-patterned ITO glass substrate was cleaned with ultrasonication in deionized water, acetone, and isopropanol for 15 minutes each. The substrates were dried under a stream of nitrogen and then treated with UV-Ozone for 15 minutes. A dispersion of the hole transport polymer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (AI 4083 Heraeus) was mixed with ethylene glycol (EG, J.T. Baker) in a 9:1 PEDOT:EG ratio by weight, and Zonyl FSO-100 (Aldrich, 5 mg Zonyl FSO-100 in 1 ml of a 9:1 PEDOT:PSS to EG mixture). The fluorosurfactant enhances the coverage of the polymer onto the films.\textsuperscript{31} Doping PEDOT:PSS with EG improves the conductivity of the polymer.\textsuperscript{146-147} This mixture was then filtered through a 0.45 \(\mu\text{m}\) polyvinylidene fluoride filter, spun-cast onto the clean ITO substrates at 4000 rpm for 60 seconds, and baked at 130 °C for 15 minutes to give a film with a thickness of 40 nm.
The mixture of PEDOT:PSS, EG, and Zonyl was utilized as prepared for the CuNi NW films, but was diluted in a 2:1 ratio with DI water for the Ag NWs because doing so resulted in higher device efficiencies. The mixture was spin coated three times (4000, 2500, 400 rpm for 1 minute each) onto pressed (80 bar, 1 minute) nanowire slides and dried under vacuum for 30 minutes. This processing resulted in film thicknesses of 52 nm and 26 nm for the undiluted and diluted EG – PEDOT:PSS, respectively.

To create the OPV active layer, previously synthesized PBnDT-FTAZ (benzo[1,2-
b:4,5-b‘]dithiophene (BnDT), fluorinated 2-alkyl-benzo[d][1,2,3]triazole (FTAZ)), and phenyl-C61-butyric acid methyl ester (PCBM) were blended together and dissolved in 1,2,4-trichlorobenzene (30 mg mL⁻¹ polymer) at 120°C overnight. The hot solution was passed through a 1 µm poly(tetrafluoroethylene) (PTFE) filter, spin coated (1 minute, 500 rpm) on the previously prepared PEDOT-coated substrates, and dried under vacuum for 20 minutes. Finally, the metal electrode (Ca 30 nm/Al 100 nm) was thermally evaporated onto the PBnDT-FTAZ:PCBM layer under vacuum (2×10⁻⁶ mbar) to complete the device.

**6.3.2. Copper Nanowire Networks With Transparent Oxide Shells That Prevent Oxidation Without Reducing Transmittance**

**6.3.2.1. Chemicals**

Sodium hydroxide was purchased from Fisher Scientific (S318-10). Copper(II) nitrate pentahemihydrate (12837), zinc chloride (429430), tin(II) chloride (208256), indium chloride (334065), ethylenediamine (EDA, E1521), 35 wt% hydrazine (N2H4) in water (309400), N, N-diethylhydroxylamine (DEHA, 471593), polyvinylpyrrolidone (PVP, 639900), and polyethylene glycol (PEG, 203910).
(PVP, MW = 10,000), ethyl acetate (270989), pentyl acetate (109584), and toluene (244511) were purchased from Sigma-Aldrich. Glass microscope slides (7.5 cm × 2.5 cm × 0.1 cm), and indium tin oxide (ITO) on glass (11 Ω sq⁻¹) were purchased from McMaster-Carr. Nitrocellulose (712) was purchased from Scientific Polymer, and acetone, ethanol and isopropanol were purchased from VWR. All chemicals were used as received. Caution should be used when dealing with these chemicals as some are corrosive (highly concentrated NaOH), flammable (N₂H₄), or dangerous if ingested or put in contact with skin.

6.3.2.2. Synthesis of Copper Nanowires

Flasks and stir bars were cleaned with concentrated nitric acid, thoroughly rinsed with deionized water, and dried in an oven at 80 °C before use. Once dry, the flasks were allowed to cool to room temperature before any reactants were added.

Cu NWs were synthesized by adding NaOH (20 mL, 15 M), Cu(NO₃)₂ (1 mL, 0.1 M), EDA (0.15 mL), and hydrazine (0.025 mL, 35 wt%) to a 50 mL round bottom flask. This mixture was swirled by hand for 5 seconds after each addition to mix the reactants. The solution was then heated at 80 °C and stirred at 200 rpm for approximately 3 minutes. After this heating step, the solution was poured into a 50 ml centrifuge tube, and a solution of PVP in water (5 ml, 0.4 wt%) was gently added to the top of the reaction solution. The centrifuge tube containing the reaction solution was placed in an ice bath for 1 hour. The Cu NWs floated to the top of the reaction solution and were
scooped into an aqueous wash solution containing N\textsubscript{2}H\textsubscript{4} (3 wt\%) and PVP (1 wt\%). The wash solution containing the Cu NWs was centrifuged at 2,000 rpm for 5 minutes, and the supernate was decanted from the Cu NWs. The NWs were then dispersed in a new wash solution (containing 3 wt\% N\textsubscript{2}H\textsubscript{4} and 1 wt\% PVP) by vortexing for 30 seconds, and then centrifuged and decanted for 3 more cycles. The Cu NWs were stored in a solution of N\textsubscript{2}H\textsubscript{4} (3 wt\%) and PVP (1 wt\%) at room temperature to prevent oxidation.

6.3.2.3. Preparation of Copper Nanowire Transparent Electrodes

Four 20 mL scale reactions were combined into one centrifuge tube after the initial washing steps. This suspension was centrifuged at 2,000 rpm for 5 minutes. The Cu NWs were washed 3 times using a solution of DEHA (1 wt\%) containing no PVP to ensure that most of the PVP was removed. After the PVP was removed, the Cu NWs were washed with ethanol to remove the majority of the water and then washed once more with an ink formulation. The ink formulation was made by dissolving nitrocellulose (0.06 g) in acetone (2.94 g) and then adding ethanol (3 g), ethyl acetate (0.5 g), pentyl acetate (1 g), isopropanol (1 g), and toluene (1.7 g). After the Cu NWs were washed with the ink formulation, another portion of ink (0.3 mL) was added to the Cu NW precipitate, and this suspension was vortexed. The final concentration of Cu NWs in the ink formulation was approximately 8 mg mL\textsuperscript{-1}.

To prepare transparent Cu NW electrodes, glass microscope slides were placed onto a clipboard to hold them down while the Cu NW ink (30 μL) was pipetted in a line
at the top of the glass slide. A Meyer rod (Gardco #13, 33.3 µm wet film thickness) was then quickly (< 1 second) pulled down over the Cu NW ink by hand, spreading it across the glass to form a thin, uniform film. The density of nanowires on the surface of the substrate could be adjusted by varying the concentration of the Cu NWs in the ink. The film was allowed to dry in air for 5-10 min followed by pressing with a shop press at a pressure of 80 bar for 1 min to lower the contact resistance between Cu NWs.

The Cu NW films were not conductive before being cleaned in a plasma cleaner (Harrick Plasma PDC-001) for 15 minutes in an atmosphere (forming gas) of 95% nitrogen and 5% hydrogen at a pressure of 600-700 mTorr to remove the nitrocellulose. The nanowire-coated glass samples were then heated at 175 °C in a tube furnace for 30 minutes under a constant flow of hydrogen (600 mL min⁻¹) to anneal the nanowires together and decrease the sheet resistance to its final value.

6.3.2.4. Preparation of Copper-Zinc, Copper-Tin, and Copper Indium Core-Shell Nanowires Transparent Electrodes

Cu NW networks were coated with Zn (Cu₉₋Zn₈) by electroplating ZnCl₂ (1 mM) in 0.1 M deaerated sodium acetate (pH ~8.2) at −1.15 V vs. NHE. Cu₉₋Sn₈ NW networks were prepared by electroplating SnCl₂ (1 mM) onto Cu NWs in 0.2 M deaerated phosphate buffer (pH 7.0) by successive CV scans between −0.10 V and −0.80 V. Cu₉₋In₈ NW networks were prepared by electroplating InCl₃ (1 mM) onto Cu NWs in 0.2 M NaCl solution at −0.75 V.
All electroplating was conducted with the model CHI601D electrochemical workstation (CH Instruments, Austin, TX). The three-electrode system consisted of a working electrode, a coiled platinum wire as the counter electrode, and a saturated calomel reference electrode (SCE, ~0.244 V vs. NHE). Freshly prepared Cu NW networks with a geometric surface area of 1-1.5 cm$^2$ were used as the working electrode. Unless stated otherwise, all electroplating was performed under deaerated conditions at 20 ± 2 °C and all potentials are reported vs. NHE.

**6.3.2.5. Characterization**

The specular transmittance and sheet resistance of NW networks on glass were measured using a UV/VIS spectrometer (Cary 6000i) and a four-point probe (Signatone SP4-50045TBS), respectively. Every reported value of the sheet resistance is the average of 5 measurements. The films were imaged with a dark field optical microscope (DFOM, Olympus BX51) to show the density, distribution, and color of the nanowires in the film. To prepare the samples for SEM (FEI XL30 SEM-FEG), a small chip of NW film on glass (5 mm × 5 mm) was placed on a piece of double sided conductive carbon tape on an SEM sample platform. The sample surface was then partially covered with carbon tape to electrically connect it to the platform, leaving a small spot uncovered for SEM imaging. To prepare the samples for bright field TEM (FEI Tecnai G² Twin), the NWs were carefully removed from the glass with a razor and dispersed in methanol by vortexing for 2 min followed by sonication for 2 seconds. 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. The same sample preparation was performed for EDS mapping (Energy dispersive X-ray spectroscopy, Super X EDS System), except that a silicon nitride grid (TEM windows, SN100-A10Q33B) was used. X-ray photoelectron spectroscopy (XPS) for elemental analysis was conducted on a Kratos Axis Ultra DLD X-rayPhotoelectron Spectrometer. The x-ray source used is monochromatic Al Kα with an energy of 1486.6 eV. The carbon 1s peak (284.6 eV) was used for internal calibration.

To measure the mass of the Cu NW film or the amount of coated metals in Cu-Ms NWs (M = Zn, Sn, or In), several pieces of as-prepared Cu NW film or Cu-Ms NW film were dissolved in concentrated nitric acid (1 ml). The dissolved Cu NWs or Cu-Ms NWs were then diluted to a set volume, and the concentrations of Cu and coated metals were analyzed using an atomic absorption spectrometer (AAS, Perkin Elmer 3100).

To test the resistance of the NW networks to oxidation, the Cu and bimetallic core-shell NW films were stored in an oven at 160 °C in air or in a humidity chamber at 85 °C/85% R.H. for different times and their sheet resistances were measured periodically.

6.3.3. Benzotriazole as an Oxidation Resistant Shell for Copper Nanowire Transparent Conductors

Nanowire film fabrication and solar cell device construction and characterization were identical to the procedures in Section 5.3.2. To coat the nanowire films with BTAH,
1% /weight of BTAH was dissolved in DI H2O in a centrifuge tube. Following acetic acid treatment and pressing to make the Cu NW films conductive, the Cu NW films were dipped in the BTAH solution for a set amount of time. Finally they were rinsed briefly (<5 seconds) with DI water to remove residual BTAH left on the substrate.

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

6.3.4.1. Copper Nanowire Synthesis

Copper nanowires (L = 28 ± 10 μm and D = 79 ± 22 nm; Cu NWs) were donated by NanoForge Corp. The nanowires 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 nanowires.

6.3.4.2. Silver Nanowire Synthesis

Silver nanowires (L = 15 ± 3 μm and D = 63 ± 7 nm; Ag NWs) were synthesized according to the polyol method 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 hour. Four solutions were then prepared: (1) 0.257 g NaCl in 20 mL EG, (2) 0.081 g Fe(NO3)3 in 10 mL EG, 1.05 g PVP (MW = 55 kDa) in 25 mL EG, and (4) 1.05 g AgNO3 in 25 mL 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 seconds between
each addition. The flask was then stoppered and the reaction was allowed to proceed at 130 °C for 7 hours. The Ag NWs were then purified with water and stored in IPA.

6.3.4.3. 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 above, 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 minutes. To produce Cu-Ag NWs with 5 nm and 15 nm thick shells of silver, 0.15 mL and 0.5 mL of 0.025 M AgNO₃ (Carolina Biological Supply Company), respectively, were added with a pipette in <1 second to the scintillation vial and the contents were left stirring for ~2-3 minutes. 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 HAuCl₄ (Aldrich) and 0.947 mL of 0.01 M K₂PtCl₆ (Aldrich) were used, respectively, instead of AgNO₃.

6.3.4.4. Nanowire Films Fabrication

Prior to preparing the transparent electrodes, the glass substrates (7.62 cm × 2.54 cm microscope slides, VWR) were sonicated in acetone for ten minutes and transferred to IPA to remove surface contaminants. The slides were wiped dry with a kimwipe and blown with air prior to NW deposition.
6.3.4.5. 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 3 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 acetone (EMD) with subsequent addition of 3 g ethanol (Koptec), 0.5 g ethyl acetate (Aldrich), 1 g pentyl acetate (Aldrich), 1 g IPA, and 1.7 g 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 nanowires 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 second) 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% N₂, 5% H₂) atmosphere for 2 minutes then placed in a tube furnace at 200 °C for 30 minutes under a constant flow of H₂ (600 mL min⁻¹).
6.3.4.6. 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 seconds (repeated twice) and DI water for 60 seconds.

6.3.4.7. 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 minutes until the NWs settled and the supernatant could be removed. The NWs were then washed twice at 2000 rpm for 2 minutes 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 minutes. The solutions were briefly vortexed (<5 seconds) between washing steps.

Films of Cu-Ag, Cu-Au, and Cu-Pt NWs were conductive immediately after coating, but a 30 second acetone rinse (repeated twice) and a 60 second 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.

6.3.4.8. Hollow Nanowire Experiments

Films of Cu NWs were fabricated as mentioned above. These films were then dipped in acetone and/or 0.58 M ascorbic acid for $2 \times 30$ seconds and $3 \times 10$ seconds, respectively, to produce the desired film of Cu NWs and dried under N\textsubscript{2} gas from an air
knife. Once dry, the films were immersed in 20 mL of 0.025 M AgNO₃ for 2 minutes 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 minute, 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 HAuCl₄ and 0.005 M K₂PtCl₆.

6.3.4.9. Oxidation Resistance

Dry oven sheet resistance (Rₛ) measurements were periodically taken with a four-point probe. Humidity chamber measurements were taken by first cutting the NW films into 1 cm × 2.54 cm pieces then defining a 1 cm × 1 cm area with silver paste and finally placing the samples in a Test Equity 200H Series Temperature/Humidity Chamber at 85 °C/85% 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 5 multimeter measurements.

6.3.4.10. 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. TEM-EDS mapping (Energy dispersive X-ray spectroscopy, 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 ~0.5 × 2.5 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 Na₂SO₄ solution was used as the electrolyte. All potentials are reported vs. Ag/AgCl unless otherwise stated. Metal concentration measurements were completed using a Perkin Elmer 3100 atomic absorption spectrophotometer (AAS). For all nanowire 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 Figures 57A and 57B are an average of 5 probe measurements.
Appendix

Table 9. Palladium Cost Calculation.

<table>
<thead>
<tr>
<th>g Cu/g Pd</th>
<th>g m⁻² Cu</th>
<th>g m⁻² Pd</th>
<th>Bulk $ Pd g⁻¹</th>
<th>$ Pd m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.2</td>
<td>0.0493</td>
<td>0.00482</td>
<td>26.6</td>
<td>0.13</td>
</tr>
</tbody>
</table>

a Determined by AAS.

b Mass of Cu per coated slide was determined by Equation A-1

\[ m_{Cu} = V_{NW} \rho_{Cu} \times \#NW \tag{A-1} \]

where \( m_{Cu} \) is the mass of copper nanowires, \( V_{NW} \) is the average volume of a nanowire determined by the average diameter and length of the nanowire and assuming a cylindrical shape, \( \rho_{Cu} \) is the bulk density of copper, and \( \#NW \) is the number of nanowires m⁻³ as determined by Equation A-2

\[ \#NW = \frac{AF}{D_{NW} L_{NW}} \tag{A-2} \]

where \( AF \) is the area covered by the nanowires per m², \( D_{NW} \) is the average diameter of the nanowires, and \( L_{NW} \) is the average length of the nanowires. Here, the fractional area coverage corresponding to a \( %T \) of 91.5 with nanowire aspect ratio \( L/D = 300 \) is roughly 0.09 m⁻².²⁴
References


39. The cost of ITO/PET films was provided by the Kintec Company of Hongkong, China (http://www.kintec.hk/). For ITO-PET films with sheet resistances/thicknesses of 10 Ω sq−1/180 nm, 20 Ω sq−1/100 nm, 25 Ω sq−1/85 nm, 50 Ω sq−1/35 nm, 80 Ω sq−1/30 nm, 100 Ω sq−1/25 nm, and 150 Ω sq−1/20 nm, their corresponding prices are $26, 17, 15, 13, 7, 6.5, and 5.5 per m2, respectively. The cost of PET film itself is $3–4 per m2. For a 100 nm-thick film of ITO, which contains 0.53 g In m−2 [100 nm (thickness) × 7140 kg m−3 (ITO density) × 90% (mass percent of In2O3 in ITO) × 82.7% (atomic weight of In in In2O3)] that costs $0.32 m−2 (0.53 g In m−2 × $600 kg−1), approximately 2.2% of the film cost can be contributed to the cost of indium [$0.32 m−2/($17-$3)].


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**Biography**

Ian Edward Stewart was born on July 31, 1990 in Ottawa, Canada. He graduated from Randolph-Macon College in May, 2012 with a B.S. degree in chemistry and minors in mathematics and music. He has published 3 peer-reviewed articles as the first author: “Solution-Processed Copper-Nickel Anodes for Organic Solar Cells” in *Nanoscale*,

“Synthesis of Cu-Ag, Cu-Au, and Cu-Pt Core-Shell Nanowires and Their Use in Transparent Conducting Films” in *Chemistry of Materials*, and “The Effect of Morphology on the Electrical Resistivity of Silver Nanostructure Films” currently under review. He is also an author on the following peer-reviewed publications: “A Rapid Synthesis of high Aspect Ratio Copper Nanowires for High-Performance Transparent Conducting Films” in *Chemical Communications*, “Copper Nanowire Networks with Transparent Oxide Shells that Prevent Oxidation without Reducing Transmittance” in *ACS Nano*, “Metal Nanowire Networks: The Next Generation of Transparent Conductors” in *Advanced Materials*, “Effects of Length Dispersity and Film Fabrication on the Sheet Resistance of Copper Nanowire Transparent Conductors” in *Nanoscale*, “Production of Oxidation-Resistant Cu-Based Nanoparticles by Wire Explosion” in *Scientific Reports*, “Synthesis and Purification of Silver Nanowires to Make Conducting Films with a Transmittance of 99%” in *Nano Letters*, and “How Copper Nanowires Grow and How To Control Their Properties” in *Accounts of Chemical Research*. He has received the following awards:
GAANN Fellowship (Duke Chemistry), Kathleen Zielek Award (Duke Chemistry) and the Duke University Graduate Program in Nanoscience Fellowship.