3D Printed Electronics



Multigram Synthesis of Cu-Ag Core–Shell Nanowires Enables the Production of a Highly Conductive Polymer Filament for 3D Printing Electronics

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This article reports a synthesis that yields 4.4 g of Cu nanowires in 1 h, and a method to coat 22 g of Cu nanowires with Ag within 1 h. Due to the large diameters of Cu nanowires (≈240 nm) produced by this synthesis, a Ag:Cu mol ratio of 0.04 is sufficient to coat the nanowires with ≈3 nm of Ag, and thereby protect them from oxidation. This multigram Cu-Ag core-shell nanowire production process enabled the production of the first nanowirebased conductive polymer composite filament for 3D printing. The 3D printing filament has a resistivity of 0.002 Ω cm, >100 times more conductive than commercially available graphene-based 3D printing filaments. The conductivity of composites containing 5 vol% of 50-µm-long Cu-Ag nanowires is greater than composites containing 22 vol% of 20-µm-long Ag nanowires or 10-µm-long flakes, indicating that high-aspect ratio Cu-Ag nanowires enable the production of highly conductive composites at relatively low volume fractions. The highly conductive filament can support current densities between 2.5 and 4.5×10^5 A m⁻² depending on the surface-to-volume ratio of the printed trace, and was used to 3D print a conductive coil for wireless power transfer.

1. Introduction

Printed electronics offers the potential to lower the cost of prototyping and producing electronics, as well as enabling the production of devices with unconventional geometries or mechanical properties (i.e., flexible and stretchable).^[1] To date, various printing methods using highly conductive inks have enabled high throughput production of RFID tags, smartcards, displays, packaging, antennas, and printed circuit boards.^[11,2] Moreover, development of electronics with unique functionalities such as wearable, flexible, and degradable sensors is now possible due to advancements in printing technology.^[3] Within the last several years, 3D printing has

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been increasingly applied to the creation of printed electronics.^[1b,i,4] The most common form of 3D printing used in consumer-grade printers involves creating a 3D object from a digital model through a layer-by-layer fused deposition modeling (FDM) process. 3D printed electronics offers the potential to prototype complex 3D objects with integrated electronics in a matter of hours versus weeks with printed circuit board-based prototyping and hand-assembly. Electronics with complex geometries that are either too costly or complicated for traditional fabrication techniques can be manufactured via 3D printing in order to improve functionality.^[1b,g,5]

Several techniques currently exist for 3D printing electronics, including hybrid insertion methods, surface direct-write, and freeform multimaterial 3D printing.^[1] Earlier methods typically use a combina-

tion of these techniques. For example, the complete fabrication of an electronic device could first start with 3D printing a nonconductive substrate, followed by filling in pre-fabricated channels with conductive ink, and finally inserting electrical components.^[1b,6] While this method has been successful in producing devices with unique configurations, it is often associated with high costs due to expensive inks that must be used with specialized printers. Moreover, there is still a need for a fabrication technique that can produce a complete device in one process from start to finish. Such a technique may be achieved by freeform multimaterial 3D printing, in which conductive and nonconductive materials can be printed side by side and a complete, functional device can be produced without disrupting the printing process. One way to achieve this is by using multimaterial FDM 3D printers, which can extrude conductive and nonconductive thermoplastics to produce 3D electronics in a layer-by-layer process.^[4c]

Due to the surge in interest in 3D printing, consumer-grade and DIY table-top 3D printers have become increasingly sophisticated while decreasing in price.^[7] Specialized conductive filaments have also been developed in a push toward printed electronics. A majority of these conductive filaments are thermoplastics containing carbon-based materials, such as carbon black and graphene.^[8] The resistivity of these filaments ranges





from 0.21 to 120 Ω cm, which means a 10-cm-long piece of filament has a resistance ranging from 1000 to 500 000 Ω . In comparison, the resistance of the same piece of copper would be 7×10^{-5} Ω . A lower resistivity (0.0026 Ω cm) has been achieved by annealing graphene nanoplatelets at 1200 °C, $^{[9]}$ but such high-temperature annealing is impractical. Electrifi, a commercially available copper-based filament, has a resistivity of 0.006 Ω cm and is compatible with even the most basic desktop printers. $^{[10]}$ While Electrifi is by far the most conductive filament that requires no post-processing techniques, there is still room for improvement. For comparison, the resistivity of bulk copper is 1.68×10^{-6} Ω cm.

We hypothesized metal nanowires with high aspect ratios could enable the production of highly conductive 3D printable polymer composites. Monte Carlo studies have previously shown that for cylinders with radius *R* and length *L*, the critical volume fraction Φ_c necessary for percolation is equal to R/L as $R/L \rightarrow 0$.^[11] This estimate becomes fairly accurate (error $\approx 2.5\%$) at L/R = 100, and the error decreases linearly with increasing L/R. The effect of aspect ratio on conductivity has been demonstrated in numerous experimental systems.^[11e,12] For example, Park et al. recently reported a thixotropic ink using silver nanowires (Ag NWs) with L/R = 133-200, and reported an experimental $\Phi_c = 0.007$, fairly close to what would be predicted based on their aspect ratio.^[12b] Thus, metal nanowires can enable the creation of highly conductive inks at low volume fractions. The low volume fraction of solid filler can in turn make it easier to ensure such conductive inks are 3D printable.

However, even though nanowires can be used at low volume fractions, creation of even a small batch of 3D printing filament for FDM printers requires tens of grams of nanowires, making the use of Ag NWs prohibitively expensive. Copper nanowires (Cu NWs) are a logical alternative, but there is no relatively green, multigram-scale synthesis for Cu NWs.^[13] One common method of synthesizing Cu NWs uses hydrazine as a reducing agent.^[13a,c] Since hydrazine is a known carcinogen, its use is undesirable for large-scale syntheses. An alternative to hydrazine is α -D-glucose, but it is a weaker reducing agent. Current reaction conditions for glucose-based syntheses involve long reaction times exceeding 6 h, and the use of an autoclave to achieve elevated temperatures (>100 °C) and pressures.^[13b,14]

In this work, we demonstrate a glucose-based, multigramscale synthesis conducted under mild and atmospheric conditions that yields 4.4 g of 45 \pm 15 μ m long Cu NWs in 1 h. Cu NWs were then coated with a thin shell of Ag at a scale of 22 g to protect them from oxidation and reduce interwire contact resistance. The Cu-Ag NWs were then incorporated into polycaprolactone (PCL) which, due to its low melting point (59-64 °C), allows the filament to be extruded at low temperatures and thereby minimizes oxidation during printing.^[15] Loading of 12 vol% Cu-Ag NWs produced the most conductive filament that could also be extruded without brittle fracture. The resulting conductive filament had a resistivity of 0.002 Ω cm, which is the lowest resistivity reported for a 3D printing filament to date. Moreover, current capacities of up to 4.74×10^5 A m⁻² could be achieved depending on the surface-to-volume ratio of the printed trace.

2. Results and Discussion

2.1. Large-Scale Synthesis of Cu-Ag NWs

Key limitations of the previous Cu NW synthesis reported by Rathmell et al. and others include (1) the use of a highly toxic chemical, hydrazine, as a reducing agent, and (2) the requirement of a large amount of NaOH (>12 M).^[13a,c,16] On the other hand, limitations of previous syntheses that use glucose as a reducing agent are (1) the requirement of elevated temperatures (>100 °C) and pressures over several hours, and (2) the resulting nanowires are coated with hexadecylamine (HDA)/ octadecylamine (ODA), making them very difficult to disperse in the aqueous solution required for silver coating.^[13b,14a,c] We have found that we can replace the hydrazine in the NaOH-EDA reaction with glucose, thereby eliminating issues with disposal of waste containing this toxic chemical. Moreover, replacing hydrazine with glucose enables the reduction of the amount of NaOH necessary for the reaction from 12 to 6.5 M. The reaction could be carried out at lower temperatures (60 °C) relative to previous syntheses using alkylamine and glucose without NaOH (>100 °C) because the conversion of glucose to reductones (the reducing agent) is accelerated in the presence of NaOH.^[14b,17] The reaction was scaled up to 10 L (Figure 1a), and was complete in only 1 h. The concentrations of the reactants used in Figure 1a are as follows: 6.5 м NaOH, 9×10^{-3} м Cu(NO₃)₂, 188×10^{-3} м EDA, and 82 mg mL⁻¹ glucose. These conditions resulted in Cu NWs that were $45 \pm 15 \,\mu\text{m}$ in length (Figure 1b) and $240 \pm 95 \,\text{nm}$ in diameter (Figure 1c). The 10 L reaction had an 85% yield and produced 4.4 g of Cu NWs.

The Cu NWs could subsequently be coated with Ag at various Ag:Cu ratios by modifying a room-temperature electroless deposition method developed by Stewart et al.^[18] In this electroless deposition process, ascorbic acid removes Cu oxide and reduces Ag ions onto the surface of the Cu NWs with minimal galvanic displacement, as well as without nucleating Ag nanoparticles in the solution. The reaction was optimized by increasing the amount of Cu NWs by a factor of 3 while keeping the concentrations of the other reactants the same, resulting in a threefold increase in production efficiency. As shown in Figure 2, the reaction was scaled up to 45 L, which yielded 22.5 g of Cu-Ag NWs in 1 h. To ensure even coating of Ag at such a large volume, AgNO3 was added at a rate of 0.5 mL s⁻¹ with a peristaltic pump. The successful coating of Ag onto the Cu NWs was verified by comparing the X-ray diffractograms of bare Cu NWs and Cu-Ag NWs (Figure 3a), which showed the appearance of Ag(111) for the Cu-Ag NWs that was not present for the Cu NWs. Scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) was performed to confirm the core-shell structure of the Cu-Ag NWs (Figure 3b,c). The element map in Figure 3b shows a copper core with a thin Ag shell. A line scan across the diameter of a Cu-Ag NW in Figure 3c shows sharp Ag peaks on both ends of the broader Cu peak, which is indicative of a core-shell structure.

Tables S1 and S2 (Supporting Information) show labor and materials cost analyses for Cu NW synthesis and Ag coating, respectively. The tables also include a list of prices





Figure 1. a) Ciruclating water bath setup for the 10 L synthesis of Cu NWs. Inset shows \approx 22 g of Cu NWs purified from the reaction. b) Dark-field optical microscopy (DFOM) image shows the Cu NWs have an average length of 45 ± 15 µm. c) An SEM image shows the Cu NWs have a diameter of 240 ± 95 nm.

for starting materials purchased at low volumes (based on prices and quantities ordered by our lab) and high volumes (more representative of a kilogram-scale manufacturing operation). Going from low volume (e.g., Sigma Aldrich) material prices to high volume material prices without changing the cost of labor decreased the price of the Cu-Ag NWs from \$16.53 to \$7.16 g⁻¹, including labor and materials costs. We note that this price does not include overhead and the cost of waste treatment and/or disposal. Further cost reduction could be obtained through reducing labor costs by increasing reaction volume, and improving the production efficiency (grams of nanowires per liter of reaction).

2.2. Stability of Cu-Ag NWs

In order to determine the optimum amount of Ag coating to produce stable and conductive NWs, Cu NWs were coated with Ag at Ag:Cu mol ratios between 0.03 and 0.07. The Cu-Ag NWs were then suspended in a nitrocellulose ink and drop-casted into thin films in wells created by double-sided tape. After heating at 150 °C for 24 h, **Figure 4**a shows the resistivity of bare Cu NWs quickly increased after 1 h until they were not conductive. Cu-Ag NWs with a 0.03 Ag:Cu mol ratio displayed an insignificant increase in resistivity, and increasing the Ag coating did not result in further improvement in stability.



Figure 2. a) Tank and pump setup for the 45 L Ag-coating synthesis. Cu-Ag NWs were collected from the bottom of the tank after settling. b) A slight color change from orange to brown can be observed after coating the Cu NWs with Ag. c) An SEM image shows the Cu-Ag NWs have a diameter of 245 ± 100 nm.



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Figure 3. a) X-ray diffractograms of Cu NWs (black) and Cu-Ag NWs (red). b) STEM-HAADF image of a Cu-Ag NW with accompanying Cu and Ag EDS maps. The scale bar is equivalent to 50 nm. c) EDS line scan across the diameter of a Cu-Ag NW showing its core-shell structure.

However, when exposed to conditions of 85 °C with 85% relative humidity (RH) for over 24 h, the sample coated with 0.03 Ag:Cu became nonconductive after 1 h (Figure 4b).

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Samples with 0.04–0.07 Ag:Cu were stable after 25 h, and increasing the Ag coating did not result in an improvement in stability in these humid conditions. Thus, a minimal amount of Ag coating (>0.04 Ag:Cu) is necessary to protect the nanowires from oxidation. Beyond this amount there is a negligible decrease in the resistivity of the films.

The mol ratio of 0.04 Ag:Cu corresponds to a shell thickness of ≈ 3 nm, which was calculated from the mol ratio and the average diameter of the Cu NWs before coating. Measurement of the Ag shell from the EDS element map shown in Figure 3b suggested a shell thickness of 5-6 nm, which is comparable to the calculated value of 3 nm. The EDS shell thickness is likely larger because the image represents a 2D projection of the pentagonal nanowire, making precise measurement of the shell thickness very difficult. Stewart et al. conducted a similar study for Cu-Ag NWs (28 \pm 10 μ m in length, 79 \pm 22 nm in diameter) and showed a minimum shell thickness of 5 nm was sufficient for preventing oxidation of Cu NWs at 160 °C for 24 h.^[18] Thus, the thickness of Ag necessary to protect the nanowires is roughly the same for the two nanowire diameters (240 vs 79 nm). However, when exposed to 85% RH/85 °C, the sheet resistance of the Cu-Ag NWs increased twofold after 24 h, unlike our results which showed no change. Additionally, since the diameter of our Cu NWs is 2.5× greater, a similar shell thickness and oxidation resistance was achieved using 73% less Ag relative to Cu. This shows that if thin nanowires are not required, using a larger nanowire diameter can reduce the amount of Ag necessary to produce oxidation-resistant Cu NWs, thereby making them more cost-effective.

2.3. Effect of Filler Morphology and Concentration on the Resistivity of the Filament

Based on previous studies of the effect of aspect ratio on conductivity of nanowire networks,[11e,12a,c,19] we expected that metal NWs with higher aspect ratios would result in a more conductive filament at a lower volume percent of filler. To test this hypothesis, we created nanowire-PCL composites with 3-25 vol% loading of 30 and 50-µm-long Cu-Ag NWs, 3-22 vol% 10 µm Ag flakes, and 3-22 vol% of 20-µm-long Ag NWs (see the Experimental Section for a detailed description of the Ag NW synthesis). Table S3 (Supporting Information) lists the dimensions of these fillers. As shown in Figure 5a, the resistivity of all samples initially declined with increasing filler fraction, but the resistivity of the nanowire composites remained nearly constant once a certain volume percent was reached (Ag NWs: 11 vol%; 30 µm Cu-Ag NWs: 9 vol%; 50 µm Cu-Ag NWs: 6 vol%). Overall, the 50-µm-long Cu-Ag NW composite had the lowest resistivity across all compositions.

We expected that the resistivity of the nanowire composites would continue to decrease with increasing volume fraction, but this did not occur. We hypothesized that this may be due to an uneven dispersion of nanowires in the composite at a larger (~mm) length scale than could be easily probed with scanning electron microscopy (SEM). Indeed, pictures of the composite films (Figure 5b) exhibit a surface roughness that increases with nanowire concentration, suggesting some degree of aggregation may be occurring. To explore this phenomenon further,





Figure 4. Stability tests (n = 3) of Cu-Ag NWs with varying mol ratios of Ag to Cu. a) Dry-oven tests at 150 °C and b) humidity chamber tests at 85 °C and 85% RH.

we performed high-resolution X-ray computed tomography (micro-CT, Nikon XTH 225 ST) on the composites. The resulting images (Figure 5c) show areas of high (red) and low (blue/black) densities of nanowires in the composite films. Aggregation is most notable in the Ag NW composite, which shows a few aggregates at 3 vol%, but more of a network of aggregates at 7 and 22 vol%. Cu-Ag NW composites similarly displayed an increased fraction of high densities of nanowires segregated into regions of the film instead of dispersed throughout the film. The aggregation in the nanowire composites makes it difficult to come to any conclusions with respect to the quantitative effects of length and aspect ratio on the conductivity in this experimental system. In contrast, the flake morphology exhibited fairly even contrast across the film, indicating a minimal amount of aggregation. At the same time, the resistivity of the Ag flake composites continually decreased.

This combination of resistivity and micro-CT data suggests that the nanowires become more easily aggregated than the flakes in the PCL composite, resulting in different resistivities as a function of volume fraction. This is likely due to the higher percolation threshold of the flakes relative to the nanowires. At volume fractions greater than Φ_c , the excluded volumes of the nanowires will interpenetrate, leading to the formation of a large number of contacts between nanowires and thus the formation of aggregates. In addition, one can intuitively expect flakes to flow across one another while nanowires may get more easily tangled.^[20] However, the resistivity of the 50-µm-long Cu-Ag NW composite at 5 vol% was lower than all other samples, including the composite with 22 vol% of Ag flake. Thus, if Cu-Ag NWs can be produced at the same cost as Ag flake (\approx \$1 g⁻¹), they can be as much as five times cheaper and achieve a lower resistivity. Tables S1 and S2 (Supporting Information) suggest that such a cost target may be within reach with further scale-up and optimization of the synthesis.

2.4. Production of 3D Printing Filament

A conductive filament was produced by adding 12 vol% 45-µm-long Cu-Ag NWs (0.10 Ag:Cu mol ratio) to PCL dissolved in dichloromethane (DCM) (Figure 6a). The DCM was evaporated off completely to form a solid composite. This composite

was cut into pellets (Figure 6b) and extruded into filament using a Filabot filament extruder (Figure 6c,d). An SEM image shown in Figure 6e suggests that the Cu-Ag NWs were evenly distributed throughout the filament at this volume fraction and length scale.

Although the previously discussed conductivity results suggest that the ideal composite would be composed of ≈5 vol% 50 µm Cu-Ag, increasing the scale of the Cu NW synthesis resulted in a slight decrease in length from 50 to 45 µm. Moreover, extruded filaments with 5 vol% Cu-Ag NWs resulted in a printable, but nonconductive, filament. The loss of conductivity after extrusion was likely caused by the breakage of wires during the extrusion step. Measurements from dark-field optical microscopy (DFOM) images of the Cu-Ag NWs in the composite before and after extrusion show the average length decreased to $10 \pm 8 \,\mu m$ (Figure S1, Supporting Information). To overcome this issue, the loading of Cu-Ag NWs was increased to 12 vol%, which was the maximum loading found to be conductive without making the filament so brittle that it could not be continuously extruded. The Ag coating was also increased to 0.10 Ag:Cu mol ratio to minimize oxidation during the elevated temperatures used during filament extrusion and printing.

The 12 vol% filament was found to be printable with a 1.0 mm nozzle at a 0.2 mm layer thickness. Printing attempts with 0.2 and 0.5 mm nozzles resulted in clogging, which is a common problem for other commercially available conductive filaments at these small nozzle diameters. Therefore, the minimum diameter and thickness of printed features with this filament are 1.0 mm and 0.2 mm, respectively.

2.5. Resistivity of Cu-Ag NW Filament

The resistivity of the conductive PCL filament was 0.002 Ω cm prior to printing (Figure 6f). This is a >100 times improvement from previously reported conductive filaments containing various carbon-based fillers such as carbon black (9–120^[8b] and 3.61 Ω cm^[8a]) and reduced graphene oxide (0.21 Ω cm^[8c]). The Cu-Ag NW filament is also comparable to the most conductive filament reported in literature, which contains graphene and has a resistivity of 0.003 Ω cm.^[9] However, the process required to reach such a low resistivity involved heating the printed object at 475 °C for 1 h to burn off the specialized polyethylene





Figure 5. a) Resistivity of filament composites containing various Ag and Cu fillers at different volume percent (vol%). b) Camera images of the composite films show the greater surface roughness of nanowire composites with high loadings of nanowires. c) Micro-CT images of filament composite films showing areas of high (red) and low (blue/black) density of metal filler. The scale bars for both (b) and (c) are 1 cm.

glycol ink, followed by an annealing step at 1200 °C for 5 min. Because our Cu-Ag NW filament does not require any postprocessing steps to achieve similar conductivity, this new filament represents a significant improvement in practicality and accessibility.

Figure 7a shows a 3D-printed inductive charging coil powering an LED using a wireless charging dock. The 3D printed coil was designed with a winding width of 2 mm and a diameter of 24 mm in order to fit within the footprint of the charging coil, giving a coil with seven turns. The inductance of this coil can be approximated with the Wheeler formula

$$L = \frac{r^2 n^2}{8r + 11w} \tag{1}$$

where *L* is inductance (μ H), *r* is the average radius of the spiral (inches), *n* is the number of turns, and *w* is the width of the winding (inches).^[21] From this formula we calculated that the inductance of the printed coil was 4.8 μ H, which is about half the inductance of the charging coil (8.7 μ H). The waveforms (Figure 7b) from the charging (transmitting) and printed (receiving) coils show 40% of the input voltage was transferred to the printed coil, which is in line with what one would expect from their difference in inductance.

2.6. Temperature Resistance and Current Capacity

Figure 8a shows the stability of 12 vol% Cu-Ag NW filament exposed to increasing temperatures in a dry oven. The resistivity of the filament was stable up to 110 °C, after which the resistivity sharply increased. At 145 °C the filament was not conductive due to the filament having melted completely at the leads. Although the filament had begun to soften at ≈ 55 °C due to the low melting point of PCL (60 °C),^[15] the resistivity of the filament was stable well beyond that point. Moreover, the areas of the conductive filament that were not in contact with the multimeter leads retained their shape throughout the duration of the experiment. These observations suggest that the Cu-Ag NW filament has a higher thermal stability than pure PCL. It is possible that the addition of Cu-Ag NWs provided structural support to the PCL by increasing the viscosity of the melt. Therefore, the PCL was able to retain its shape, and the connections between the Cu-Ag NWs were maintained beyond the expected melting point.

The maximum current capacity of the 3D printed traces was determined by plotting the current density at failure for printed traces with varying surface-area-to-volume ratios, as shown in Figure 8b. The current was increased stepwise in 1 mA increments every 5 s. Failure was defined as the current at which the resistance of the trace doubled due to Joule heating, which caused the PCL to melt and the Cu-Ag NWs to oxidize.

To estimate the current density at failure for the printed traces, we assume homogenous Joule heating, heat conduction along the printed traces, and heat conduction from the printed traces to the surrounding air via convection. The temperature distribution T(x) in the printed trace is given by Equation (2)







Figure 6. a) Filament production started with a mixture of Cu-Ag NWs and PCL dissolved in DCM. b) Drying of this solution created a solidified composite which was cut into uniform pellets, and c) extruded through a Filabot to form the filament. d) The Filabot produced a coil of conductive filament similar in dimensions to other commercially available filaments used for 3D printing (diameter = 1.75 mm). e) SEM image shows the dispersion of Cu-Ag NWs in the PCL filament. f) A 90 mm length of filament with a diameter of 1.8 mm had a measured resistance of 0.7 Ω .

$$T(x) - T_{\infty} = \frac{j^2 \rho V}{A_{SA} h} \left[1 - \frac{\cosh\left(x \sqrt{\frac{A_{SA}}{V} \times \frac{h}{K}}\right)}{\cosh\left(\frac{L}{2} \sqrt{\frac{A_{SA}}{V} \times \frac{h}{K}}\right)} \right]$$
(2)

where T(x) is the temperature of the printed trace at x, T_{∞} is the temperature of the air in the room, j is the current density, ρ is the resistivity of the printed trace, K is the thermal conductivity of the printed trace, L is the length of printed trace, x is the position along the length of the trace $(-L/2 \le x \le L/2$ and x = 0 at the middle of printed trace), h is the heat transfer coefficient, A_{SA} is the surface area of the trace, and V is the volume of the printed trace.^[22] Based on this equation, the highest temperature occurs at the middle of the printed trace. This is indeed what occurred when we applied a current to the printed traces which was increased stepwise in 1 mA increments every 5 s (see Figure 8b). Thus, in order to predict the current density at failure, it is only necessary to determine the change in



$$T(0) - T_{\infty} = \frac{j^2 \rho V}{A_{\rm SA} h} \left[1 - \frac{1}{\cosh\left(\frac{L}{2}\sqrt{\frac{A_{\rm SA}}{V} \times \frac{h}{K}}\right)} \right]$$
(3)

Equation (3) can be simplified further since the term $\frac{L}{2}\sqrt{\frac{A_{SA}}{V}} \times \frac{h}{K} \gg 1$. For our experimental conditions, the values of A_{SA}/V are in the range of 2400–4300 m⁻¹ and the length of the traces are 0.025 m. A typical heat transfer coefficient (*h*) for air with natural convection is 200 W m⁻² K⁻¹, and the thermal conductivity (*K*) of metal NW-polymer composite is below 2 W m⁻² K⁻¹.^[22,23] Thus, the bracketed term is ≈1 (i.e., 0.996–0.999) and Equation (3) can be simplified to

$$T(0) - T_{\infty} = \frac{j^2 \rho V}{A_{SA}h} \tag{4}$$

By simply rearranging Equation (4), the current density of the printed trace at failure (j_{failure}) due to Joule heating can be expressed as

$$j_{\text{failure}} = \sqrt{\frac{h\Delta T_{\text{at failure}}}{\rho}} \cdot \sqrt{\frac{A_{\text{SA}}}{V}}$$
(5)

Equation (5) shows a linear relationship between the current density at failure and the square root of the surface-area-to-volume ratio, where the slope is dependent on the heat transfer coefficient, the difference in the temperature of the printed trace, the air in the room ($\Delta T_{\rm at\ failure}$), and the electrical resistivity of the trace.



Figure 7. a) Demonstration showing how the Cu-Ag NW filament can be used to 3D print an inductive charging coil to wirelessly power an LED. b) Oscilloscope measurement of the transmitted (charging coil) and received (inductor coil) waveforms.





Figure 8. a) Resistivity of the conductive filament vs temperature. The melting points of pure PCL and PCL with Cu-Ag NWs are indicated by dashed lines. b) 3D printed traces before (top) and after (bottom) failure due to Joule heating. c) Current density at failure with the square root of the surface-to-volume ratio of the 3D printed traces.

Figure 8c shows that a plot of $j_{\rm failure}$ versus $\sqrt{\frac{A_{\rm SA}}{V}}$ is linear, as expected from Equation (5). The validity of the experimental data was further verified by setting $\Delta T_{\rm at\,failure} = 85$ K based on the difference between the temperature of the filament at failure and room temperature, and $\rho = 0.00004 \ \Omega$ m based on the average resistivity

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of the printed traces. With these variables known, the convective heat transfer coefficient could be determined from the slope of the experimental linear fit. The calculations resulting from the experimental data indicate the heat transfer coefficient was 79 W m⁻² K⁻¹. Previous work on heat transfer in an additively manufactured polymer heat exchanger reported a heat transfer coefficient range of 35–120 W m⁻² K⁻¹,^[24] in line with that of the experimental data. Such a predictable trend is helpful in engineering the geometry of a 3D printed object based on the current that will be applied. Not surprisingly, a printed trace with a higher surface-area-to-volume ratio, a lower resistivity, and a higher melting point polymer will withstand a higher current density.

3. Conclusion

In conclusion, we have developed a multigram-scale synthesis of Cu NWs that eliminates the need for hydrazine, reduces the amount of NaOH required for the reaction, and can be carried out at 60 °C in 1 h. These nanowires were then coated with Ag in a 22 g scale reaction. By tuning the molar ratio of Ag:Cu, we found that only 4 mol% Ag (corresponding to a shell thickness of \approx 3 nm) was necessary to protect the nanowires from oxidation. Blending of Ag flakes, Ag NWs, and Cu-Ag NWs into the composite showed that a 5 vol% composite with 50- μ m-long CuNWs was more conductive than composites containing 22 vol% Ag NWs, Ag flake, and Cu-Ag NWs with smaller dimensions, thus demonstrating the powerful effect of aspect ratio on composite conductivity. Cu-Ag NWs were used to create a 3D-printing filament >100 times more conductive than commercially available graphene-based filaments. Printed traces were stable up to 110 °C, limited by the low melting point of the PCL filament (60 °C), and could support current densities between 2.5 and 4.5 \times 10^5 A m^{-2} depending on the surfaceto-volume ratio of the printed trace. A 3D-printed inductive charging coil provided a simple demonstration of the potential applications of the highly conductive Cu-Ag NW filament. It appears the aggregation of the nanowires in the filament limited the maximum conductivity that could be achieved. Thus, future work on nanowire composites might further explore the effect of nanostructure morphology and surface treatment on aggregation and the rheology of the polymer melt during processing to achieve higher loadings of nanostructures.

4. Experimental Section

Cu NW Synthesis: To synthesize Cu NWs with an average length of 45 \pm 15 μ m and diameter of 240 \pm 95 nm in a 10 L reaction, Cu(NO₃)₂·2.5H₂O (800 mL, 0.1 M, Sigma Aldrich, ≥98.0%), NaOH (7.5 L, 8 M, NOAH Technologies, 99.0%), and 115 mL of ethylenediamine (115 mL, EDA, Sigma) were combined and shaken by hand after each addition (Note: make sure to wear personal protective equipment suitable for handling highly basic solutions in case of spills, e.g., face mask, rubber apron, and elbow length rubber gloves). After these solutions were mixed, α -D-glucose solution (750 mL, 1 g mL⁻¹, Sigma Aldrich, 96%) was added to the reaction solution, mixed by shaking, and immediately placed in a 60 °C water bath for 1 h. Once the reaction was finished, Cu NWs were separated from the reaction solution using a stainless-steel mesh strainer. The Cu NWs were resuspended in an aqueous solution (400 mL)

containing 3 wt% polyvinylpyrrolidone (Sigma Aldrich, avg MW 10 000) and 1 wt% *N*,*N*-diethylhydroxylamine (TCI America, >95.0%) (PVP/DEHA). The resuspended NWs were purified through gravity filtration using a custom-made funnel fitted with a stainless-steel mesh (30 μ m pore size). The wires were rinsed three times with aliquots of PVP/DEHA (250 mL) while a stirring force was applied during filtration. The resulting "slush" of Cu NWs was stored in PVP/DEHA at a concentration of 4.5 mg mL⁻¹. Repeating this process five times produced \approx 22 g of Cu NWs for coating with Ag.

Cu NWs with an average length of 50 μ m and diameter of 230 nm were synthesized by sequentially adding Cu(NO₃)₂·2.5H₂O (160 mL, 0.1 M), NaOH (1500 mL, 8 M), and EDA (23 mL) in a 2 L glass Pyrex bottle and thoroughly shaking by hand after each addition. After these solutions were mixed, α -D-glucose (150 mL, 1 g mL⁻¹) was added to the reaction solution, mixed by shaking, and immediately placed in a 60 °C oven for 4 h. Cu NWs with an average length of 30 μ m and diameter of 120 nm were synthesized by increasing the amount of glucose to 250 mL and keeping all other reaction parameters the same. Once the reaction was finished, the Cu NWs were purified by first decanting out 80% of the reaction solution, then precipitating the Cu NWs via centrifugation at 2000 rpm for 10 min. The supernatant was discarded, and the Cu NWs were resuspended in PVP/DEHA (\approx 200 mL), vortexed for 30 s, and centrifuged again. This rinsing process was repeated three times before storing the Cu NWs in PVP/DEHA at a concentration of 1.6 mg mL⁻¹.

Cu-Ag NW Synthesis: A total of 22 g of Cu NWs were coated with Ag by combining Cu NWs in PVP/DEHA (5 L, 4.5 mg mL⁻¹), PVP solution (10 L, 4 wt%), and L-ascorbic acid (27.5 L, 1 M, Duda Energy, >99.0%) in a 15 gallon inductor tank. This solution was stirred with an overhead stirrer for 15 min under ambient conditions. A peristaltic pump was used to add AgNO₃ (1416 mL, 0.025 M, Fisher Scientific, ≥99.7%) at 0.5 mL s⁻¹ as the reaction solution continued to stir. The reaction solution was stirred for an additional 5 min after the complete addition of AgNO₃, then purified through a custom-made funnel fitted with a stainless-steel mesh (30 μ m pore size). The Cu-Ag NWs were rinsed three times with deionized H₂O, then further purified through centrifugation (2000 rpm, 10 min) three times with methanol (VWR, ACS).

Cu-Ag NWs with varying Ag:Cu mol ratios were synthesized in a smaller scale reaction by adding Cu NWs in PVP/DEHA (2 mL, 1.6 mg mL⁻¹) to a solution of L-ascorbic acid (5.5 mL, 1 M) and PVP (2 mL, 4 wt%), and stirring for 5 min. Varying amounts of AgNO₃ (0.025 M, 0.03 mol ratio: 60 μ L, 0.04 mol ratio: 80 μ L, 0.05 mol ratio: 100 μ L, 0.06 mol ratio: 120 μ L, and 0.07 mol ratio: 140 μ L) were added to the reaction solution and stirred for 3 min. The resulting Cu-Ag NWs were purified by precipitating the NWs via centrifugation (2000 rpm, 10 min) and resuspending in PVP/DEHA three times.

Samples for X-ray diffraction (XRD) analysis were prepared by centrifuging and resuspending Cu and Cu-Ag NWs in isopropanol. The solutions were drop-casted into circular wells created using double-sided tape, dried in a nitrogen box, and analyzed using a Panalytical X'Pert PRO MRD HR. Samples for STEM-EDS were prepared by resuspending Cu-Ag NWs in deionized H_2O , and depositing a drop of the suspension onto holey carbon TEM grids (Ted Pella). Images were obtained with an FEI Titan 80-300.

Stability of Cu-Ag NWs: Cu NWs and Cu-Ag NWs (0.3–0.7 mol ratio Ag:Cu) were dispersed in nitrocellulose ink (1 mL). Varying amounts of NW-ink solution containing 0.64 mg of Cu-Ag NWs were drop-casted into circular wells created by double-sided tape and dried completely. One set of samples was placed in a 150 °C drying oven for 24 h, and resistivity was measured with a four-point probe. Another set of samples was trimmed into rectangles. Ag paste was applied to the ends of the rectangular samples, and the samples were placed in a humidity oven set to 85 °C/85% RH for 24 h. Resistance was measured with a multimeter. Resistance was converted to resistivity by measuring the exact dimensions of the drop-cast samples using a caliper and micrometer.

Ag NW Synthesis: Ag NWs with an average length of 20 μ m were synthesized based on the polyol method.^[25] Ethylene glycol (158.4 mL, J. T. Baker) was added to a 500 mL round-bottom flask and heated to 125 °C in an oil bath for 30 min. The following solutions were then prepared: (1)

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NaCl (0.257 g, Fisher Scientific) in ethylene glycol (20 mL), (2) $Fe(NO_3)_2$ (0.081 g, Sigma Aldrich) in ethylene glycol (10 mL), (3) PVP (1.05 g, MW = 55 000, Sigma Aldrich) in ethylene glycol (25 mL), and (4) AgNO₃ (1.05 g, Fisher Scientific) in ethylene glycol (25 mL). Solution 1 (0.2 mL), solution 2 (0.1 mL), solution 3 (20.76 mL), and solution 4 (20.76 mL) were sequentially added to the preheated round-bottom flask while stirring at 150 rpm. After 5 min, the temperature of the oil bath was increased to 130 °C, and the reaction was allowed to progress for 6 h. The resulting Ag NWs were purified by precipitating the NWs via centrifugation (1000 rpm, 20 min) and rinsing with acetone (VWR) three times.

Composition versus Resistivity: Drop-cast filament composites were prepared to test the effect of Cu-Ag NW, Ag NW, and Ag flake composition on resistivity. PCL (1 g) was dissolved in DCM and Cu-Ag NWs, Ag NWs, or Ag flakes (Aldrich, \geq 99.9%, 10 µm) were added to make samples containing 3–25 vol% filler. The composite solutions were cast into silicone wells and allowed to dry. Nonuniform edges were trimmed off and two small strips of Ag paste were applied to opposite ends. Resistance measurements were taken using a multimeter and were converted to resistivity by measuring the exact dimensions of the samples using a caliper and micrometer.

Cu-Ag NW Filament Production: Cu-Ag NWs and PCL were combined in a 12:88 volume ratio to make the filament composite. First, Cu-Ag NWs (22 g) in methanol were resuspended in dichloromethane (1.5 L, VWR, ACS) via centrifugation. PCL pellets (22 g) from IC3D Printers, LLC were added to the NW solution while stirring rapidly. The composite solution was stirred for 1 h to ensure the PCL dissolved completely. The composite solution was poured into a glass tray and stirred every few minutes to maintain a homogenous dispersion of wires while most of the DCM evaporated. Once the composite was viscous enough to maintain its shape, it was spread out to create an \approx 5 mm thick sheet, and was dried in the hood overnight. The resulting solid slab of NW/PCL composite was cut into smaller pellets (5 × 5 mm) and further dried in a 50 °C oven for 2 h. The dried pellets were fed into a Filabot filament extruder set to 120 °C and fitted with a 1.6 mm nozzle.

3D Printing of Cu-Ag NW Filament: A 3D model of the inductive charging coil was created using Fusion 360, then converted to a 3D printable gcode using Cura 3D printing slicing software. A HICTOP Prusa I3 fitted with a 1 mm nozzle was used to print the coil at a printing speed of 15 mm s⁻¹ and extrusion temperature of 160 °C. Alligator clips were used to attach the LED to both ends of the coil, which were coated with silver paste to reduce contact resistance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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