Electrical and mechanical properties of high electrical conductivity CNT/Cu-yarns with Br doping and Cu encapsulation

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Abstract
Carbon nanotubes (CNTs) are an ideal starting material for the development of strong, light-weight conductors. In this work, we pursued the development of high specific electrical conductivity and high specific strength CNT/metal composites. We started with CNT yarns which had an initial electrical conductivity, $\sigma_e$, of 3.14 MS m$^{-1}$ and a density of 1.32 g cm$^{-3}$. We brominated the yarns, demonstrating increases in $\sigma_e$, with our best samples reaching $\sigma_e = 7.00$ MS m$^{-1}$. To increase the stability of the bromination, we electroplated a Cu layer onto the Br-doped yarn which led to a stabilization of the conductivity improvement. This was quantified by monitoring periodically the $\sigma_e$ of a Br-doped and metallized CNT yarn over a period of 69 days, during which time the sample was otherwise exposed to ambient conditions. Analysis gives a value 6.15 MS m$^{-1}$ for the brominated yarn after metallization which is excellent for CNT yarns. Tensile tests on these Cu/CNT composites showed tensile strengths reaching 700 MPa, Young’s modulus values of 22.8 GPa, and specific tensile strength values of 146 kN*m kg$^{-1}$ (this latter is 6X that of Cu). Our best CNT-Cu composites show specific conductivity values comparable with that of Cu but with much higher specific tensile strengths.

KEYWORDS
carbon nanotube, composite conductor, dopants stabilization, high specific conductivity, high specific strength

1 | INTRODUCTION

Ever since carbon nanotubes (CNTs) were first characterized in 1952,[¹] there have been sustained research efforts exploring various aspects of their fabrication, properties, and applications. This sustained attention has been due to CNTs’ unparalleled charge mobility, high strength, and high modulus. Single-walled CNTs (SWCNTs), with a measured field-effect mobility of $\sim$8000 cm$^2$ V$^{-1}$s$^{-1}$ at room temperature and an intrinsic mobility greater than...
$10^5 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$, have been of interest for use in high-speed field-effect transistors, as well as other active devices. However, since charge mobility can be regarded as carrier density normalized $\sigma_e$, CNTs are also potentially excellent conductors if additional charge carriers are introduced. High strength, high conductivity, light weight conductors are of great interest technologically, with programs funded by NASA, the Air Force, the Navy, and the US Department of Energy. Some of the applications of interest include high power density motors and generators for transport and propulsion, as well as reducing the weight of aircraft. Aircraft have a significant weight coming from wiring, which may increase with propulsion electrification. However, there are many applications where light, strong, and high conductivity wires would be important.

The mass density of CNTs is low, ranging from $\sim 1.2 \text{ g cm}^{-3}$ for SWCNTs to $\sim 1.8 \text{ g cm}^{-3}$ for multi-walled nanotubes (MWCNTs). Although the reported values for Young’s modulus ($E$) and ultimate tensile strength (UTS) of CNTs vary, individual CNTs are generally very stiff, with an $E$ ranging from 1-5 TPa for SWCNTs and an average of 1.8 TPa for MWCNTs. With an UTS ranging from 11 to 63 GPa for SWCNTs and an average of 1.72 GPa for MWCNTs, CNTs are also strong. Because of these mechanical and electrical properties, CNTs are a desirable lightweight and electrically conductive reinforcement/material for making a multitude of composites.

In our study, CNT yarn from DexMat, with a $\sigma_e = 3.14 \text{ MS m}^{-1} \pm 0.8\%$ and density of $1.32 \text{ g cm}^{-3} \pm 1.6\%$, was doped with Bromine. Br is an electron acceptor for CNTs and this doping (bromination) treatment of the CNT yarn was performed to improve the electrical conductivity, $\sigma_e$, of the yarn; we were able to reach $7.00 \text{ MS m}^{-1} \pm 7.2\%$. Recent results have shown values as high as $8.5 \text{ MS m}^{-1}$ using very high aspect ratio (i.e., “long”) CNTs as starting materials, and we anticipate that bromine doping could push this value even higher. In our studies below, the bromination does increase the density of the as received yarn, in this case to $1.55 \text{ g cm}^{-3} \pm 6.9\%$.

Such brominated yarn can handle nearly double the current density of the as-received yarn (as quantified in terms of ampacity), both the brominated yarn and as-received yarns failing at the limiting current densities due to localized joule heating. However, bromination is not an intrinsically stable dopant for CNT yarns, even for service at room temperature. To enhance the long-term stability of bromination and thus, the maximum ampacity of the conductor via delocalization of joule heating, Cu electrodeposition was performed on brominated CNT yarns. A reel-to-reel Cu electrodeposition system was constructed and utilized to make a continuous long CNT yarn-Cu composite wire. Our work explores the effect of Cu metallization on CNT yarns, the CNT-Cu interphase boundary, and the electrical and mechanical properties of this CNT yarn/Cu composite. Our goal is to combine the merits of CNT yarn with those of Cu in order to fabricate a light-weight, high-strength, highly conductive composite wire.

## EXPERIMENTAL SECTION

A single-zone bromination process, similar to that used by Endo et al., was applied to dope CNT yarns obtained from DexMat. For the first series of experiments, “nominally undoped” DexMat yarn was used. The CNT wire was placed into a flask where a small amount of liquid Br was added, and an inert gas (Ar) was streamed into the flask at 100 sccm. The exhaust was connected to a condensation unit where Br vapor could condense and be recollected in a separate flask. The entire setup was placed in the fume hood and the process was conducted at room temperature under which condition the vapor pressure is sufficient for Br$_2$ intercalation.

The Cu plating electrolyte had ratios of 1:1.6:11.7 for the CuSO$_4$·5 H$_2$O: H$_2$SO$_4$: H$_2$O constituents. The CNT yarn and an OFHC Cu plate were used as cathode and anode, respectively, during the electroplating process. The applied current density was 20 mA cm$^{-2}$, under which conditions both the formation of insoluble oxide (cupric oxide) on the anode as well as the buildup of Cu in the bath solution could be avoided. The thickness of the Cu layer was controlled by the electrodeposition dwell time via the reel-to-reel process feed rate. The weights of the as received yarn, the brominated yarn, and Cu-plated yarns were measured with a Mettler Toledo XPR26 analytical balance. Each sample was measured five times to obtain an average mass value as well as an error estimate.

Electrical conductivity tests were performed on the samples via a standard four-point measurement technique using an HP614A precision power supply in conjunction with a Keithley 2182A nanovoltmeter. Five kinds of yarns/composites were tested, including S1 (As-received yarn), S2 (Brominated yarn), S3 (As-received Cu-plated yarn), S4 (Brominated yarn with thin Cu plating), and S5 (Brominated yarn with thick Cu-plating). S1 and S2 were measured at 0.3 A, while S3, S4, and S5 were measured at 1 A. For each yarn/composite type, three to five samples were measured, and for each sample, three measurements were performed. These values were then used to obtain the average value of $\sigma_e$ as well as its standard error. The maximum ampacity measurement for each sample was taken only once due the destructive nature of this experiment. We also explored the time stability of the Bromine doping by measuring the $\sigma_e$ of selected samples after set intervals with the samples exposed to ambient conditions.
TABLE 1 Sample processing and performance tests

| Sample ID | Processing | Analyses               |
|-----------|------------|------------------------|
| S1        | As-received yarn (“bare,” undoped) | Density, $\sigma_e$, and tensile testing |
| S2        | Brominated yarn | Density, $\sigma_e$, and tensile testing |
| S3        | As-received yarn with Cu-metallization | Density, $\sigma_e$, SEM, EDS |
| S4        | Brominated yarns/thin Cu metallization | Density, $\sigma_e$, tensile testing, SEM, EDS |
| S5        | Brominated yarns/thick Cu metallization | Density, $\sigma_e$, tensile testing, SEM, EDS |
| S6        | Manufacturer pre-doped yarn | $\sigma_e$ versus $T$ |
| S7        | Manufacturer pre-doped yarn/Cu metallization | $\sigma_e$ versus $T$ |

The as-received yarns “bare” yarns have in fact a modest level of p-type doping from the baseline CNT manufacturing process.

Mechanical testing was performed on S1-S5 using an MTS load frame in conjunction with FCH203A-Manual Capstan bollard grips to avoid failure at the gripping point. The testing procedure was based on ASTM standard A931-08, B986-13, and C1557-14. Each measured sample had a total length of 45 cm and a gauge length of 17 cm. Uniaxial tensile tests were performed using a strain rate of 0.1 in min$^{-1}$ (0.254 cm min$^{-1}$).

In a second set of experiments, we set out to explore the temperature stability of doped CNT yarn. In this case we used manufacturer pre-doped (via a proprietary process) yarns, exploring the temperature stability of this pre-doping with and without Cu metallization. We used two further sample types, S6 (manufacturer pre-doped yarn) and S7 (manufacturer pre-doped yarn with Cu metallization) and tested their $\sigma_e$ at elevated temperatures. Electrical conductivity versus temperature measurements were performed under a controlled atmosphere of 80/20 Ar/H$_2$. The samples were heated from room temperature to 280°C at 10°C min$^{-1}$ and $\sigma_e$ was measured using a four-point technique. Table 1 summarizes the different processing methods used for each yarn/composite as well as the performance tests applied.

3 | RESULTS AND DISCUSSION

The as-received yarn (S1) consisted of 49 CNT fibers (sub-yarns) bundled together to form a final yarn with an average cross sectional area of 23,000 $\mu$m²±3.7%, as presented in Table 2. After bromination the yarn (S2) cross sectional area was unchanged, at 23,000 $\mu$m²±6.8% (Table 2). To determine this total yarn area, the cross-sectional area of sub-yarns (fibers) were measured using SEM, and the total CNT yarn cross section was calculated as the average size of the individual CNT fiber x 49. To perform this analysis, the areas of 15 sub-yarns of the as-received sample and 30 sub-yarns of the brominated samples were measured from SEM images. The average area values as well as their standard errors were taken from these measurements. We note that previous studies using Br$_2$ to form a graphitic intercalation compound have shown a dimensional change of the structure.[16,21] However, there is no noticeable size increase for the brominated CNT yarns, because, as shown Figure 1, the CNTs are not perfectly dense within the fiber, leaving free spaces to accommodate the Br$_2$ intercalation.

Figures 2–4 present the SEM results for S3, S4, and S5. The EDS phase mapping results are shown for all samples, and in general it can be seen that the Cu-plated yarns contain, in addition to an outer Cu region and an inner CNT fiber core, a distinct Carbon-Cu interface region as well as minor voids. The Carbon-Cu interface regions have a thickness $\approx$0.8 $\mu$m. Within this interface region, the space between CNT fibers is filled with a Cu-CNT interphase material, and the weaving structure of the CNT yarn affects the relative fractions of the Cu-CNT interphase material per unit length of Cu-CNT composites. Table 2 lists the densities and filling fractions for CNT, Cu, and interphase materials for the various composites, based on SEM analyses. Six cross-sections were taken along the composite for S3 and five cross-sections were taken for S4 and S5. The average area and standard error of each phase were...
TABLE 2  Sample densities and fill fractions of CNT, Cu, and interphase materials

|      | Cross sectional area [µm$^2$] | Density [g cm$^{-3}$] | Interphase density (g cm$^{-3}$) | CNT%$^a$ | Cu %$^a$ | Inter-phase %$^a$ |
|------|-------------------------------|-----------------------|-----------------------------------|------------|----------|------------------|
| S1   | 23,000±3.7%                   | 1.32±3.9%             |                                   |            |          |                  |
| S2   | 23,000±6.8%                   | 1.55±6.9%             |                                   |            |          |                  |
| S3   | 88,700±1.5%                   | 6.67±2.0%             | 5.36±2.5%                         | 26.0±1.5%  | 68.3±1.5% | 5.61±1.5%        |
| S4   | 43,800±8.5%                   | 4.82±8.6%             | 6.81±12.1%                        | 52.6±1.5%  | 36.7±1.5% | 10.5±1.5%        |
| S5   | 71,900±1.2%                   | 6.32±1.8%             | 7.04±2.2%                         | 32.0±1.5%  | 54.8±1.5% | 13.0±1.5%        |

$^a$The error is estimated at 0.5% for the SEM analysis here.

FIGURE 2  A, SEM images for S3 (Non-brominated Cu-plated yarn); B, EDS scanned area; C, EDS phase mapping; D, EDS spectrum of CNT area; E, EDS spectrum of interphase area

FIGURE 3  A, SEM images for S5 (Brominated yarns with thick Cu-plating); B, EDS scanned area; C, EDS phase mapping; D, EDS spectrum of CNT area; E, EDS spectrum of interphase area
extracted for each wire based on these measurements. Our estimate of reading error in the SEM area analysis is <0.5% for these measurements. From previous work, we know that the continuous Cu-plating process can provide a uniform Cu encapsulation along the CNT yarn with a standard error for these dimensions of \( \approx 1\% \). However, it can be noticed that the standard errors of S2 and S4 are larger than those of S3 and S5. This may be associated with the bromine doping process, although S5, which is brominated, but has a thicker Cu plating, has also a smaller area variation. We list then the area fractions of CNT, Cu, and the interphase region. Like the errors listed for the total cross sectional area, the error for these quantities is dominated by the sample variability and not the measurement error. However, we interpret the variability to be variations in the level of radial compaction in the yarn. That is, we take the number of CNTs crossing the plane in a cross section to be relatively fixed, with the variations in CNT yarn area to be due to variable levels of void area within the CNT weave. This affects the error bars for the quoted CNT conductivities below, but is consistent with the high reproducibility of the resistance (conductance) measurements which we detail below. According to the rule of mixtures, the density of the interphase materials in S3, S4, and S5, are calculated to be 5.36, 6.81, and 7.04 g cm\(^{-3}\), respectively.

In Figure 2A we see the SEM of S3, an un-brominated but Cu plated yarn. Figure 2B shows a higher resolution image of the individual sub-yarn and the interface it forms with the Cu metallization. Figure 2C shows an EDS map with the Cu, CNT, and interface regions distinguished by false-color. In Figure 2D we see the spectrum for the CNT region of S3, which shows that in addition to Cu and C, oxygen, chlorine, and sulfur are also present. These impurities are likely introduced during the CNT yarn fabrication process (which involves the use of chlorosulfonic acid), the Cu electrodeposition process, and finally oxidation at defect sites of the CNTs and on the Cu surfaces after sample preparation. Figure 2E shows the EDS spectrum for the interface region, showing Cu, O, and C predominantly.

Figure 3 shows SEM, EDS mapping, and the EDS spectrum for S5, the brominated yarn with a thick Cu electroplating. The results are very similar to those of S3 (Figure 2), except that Br is seen both in the CNT region as well as the Cu electroplating region.
TABLE 3 Electrical properties of S1-S5

|    | $\sigma_e$ [MS m$^{-1}$] | Ampacity (maximum current density) [A cm$^{-2}$] | $\sigma_{e,m}$ [S m$^{-2}$ kg$^{-1}$] | CNT $\sigma_e$ after Cu-metallization [MS m$^{-1}$] $^b$ |
|----|-----------------|---------------------------------|-----------------|--------------------------------------|
| S1 | 3.14±4.2%       | 4.00±10$^3$±3.7%                | 2390±5.7%       |                                        |
| S2 | 7.00±7.2%       | 7.24±10$^3$±6.8%                | 4510±10.0%      |                                        |
| S3 | 40.3±1.9%       | 20.5±10$^3$±1.5%                | 5960±2.8%       | 2.57±1.9%                            |
| S4 | 24.5±8.9%       | 33.8±1.8%                       | 5090±12.4%      | 6.13±8.9%                            |
| S5 | 18.3±1.3%       | 18.3±10$^3$±1.2%                | 5340±2.5%       | 6.17±1.8%                            |

$^a$Errors listed in this table combine electrical measurement error and area standard error (area variation), but are dominated by area standard error (variation) as given in Table 2.

$^b$Here the errors are applied to the final value of the result, since the conductance/resistance measurement errors are quite small, and the error is propagating through the area in terms of the final quoted value.

Figure 4 shows the results for S4, which are very similar to those for S5 (Figure 3), except that in Figure 4E-G, we see the EDS spectrums corresponding to several layers of the interface region. This scan was taken at high resolution, and here we see for this sample that the CNT-Cu interphase is comprised of three layers, displayed as red, green, and orange from inner to outer layers. In addition, the signal strength of Br, S, and Cl in the interphase region decreases as a function of distance from the CNT region, and this should lead to a diffusion barrier effect of the interphase with respect to those doping elements, as discussed further below.

We note that Br$_2$ intercalation is one of most effective intercalation species for increasing the $\sigma_e$ of CNTs by generating charge carriers,[22,23] but as an exohedral, non-covalent dopant it suffers from instability at room temperature.[23,24] We measured the as-received CNT yarn to have an $\sigma_e$ of 3.14 MS m$^{-1}$±4.2%. After bromination, S2 was found to have a significant increase, with $\sigma_e = 7.00$ MS m$^{-1}$±7.2%. In order to obtain these results, multiple samples were measured and multiple measurements per sample were performed. For S1 and S2, five different samples were measured for each, and each of these samples was measured three times. For samples S3, S4, and S5, three different samples were measured for each type, and three measurements per sample. These results are given in Table 3. This is a very significant increase in $\sigma_e$, and clearly indicates not only an increase in the $\sigma_e$ of the CNTs themselves, but an improvement for the yarn overall. One possible reason for this might be that Br not only serves as an acceptor but also lowers the contact barrier between CNTs of different chiralities, diameters, and wall-counts to decrease the overall resistivity of the yarn.[12] According to Maarouf, et al., the Br$_2$ doping makes it easier for the charge carriers to transfer between CNTs with different diameters and chiralities by relaxing the constraint of the momentum conservation along the tube direction.[25] The increased density of S2 compared with S1 was also caused by the Br$_2$ intercalation. The $\sigma_e$ of S2 was monitored over a period of 69 days, during which time the sample was otherwise exposed to ambient conditions. The (room temperature) $\sigma_e$ of S2 showed an exponential decay with respect to time, decreasing from 7.00 MS m$^{-1}$±7.2% to 5.28 MS m$^{-1}$±7.2% in 69 days, as shown in Figure 5A. Having anticipating this volatility, we also monitored the $\sigma_e$ versus time for samples (S4 and S5) which had been brominated and then Cu plated. Figure 5A shows the results for $\sigma_e$ versus time for S2, S4, and S5, where S4 and S5 show constant conductivities of 24.5 MS m$^{-1}$±8.9% and 33.8 MS m$^{-1}$±1.8%, respectively, as listed in Table 3. For S2 the direct $\sigma_e$ is given, while for S4 and S5, the value for the CNT is extracted from that of the composite by analysis. All samples were measured multiple times for each of the data points in Figure 5A and the reproducibility of the $\sigma_e$ measurement was seen to lead to an error below 0.5%. We note that some additional variability is seen for S2 as a function of time. Even though multiple measurements on the same day led to an error <0.5%, this may be associated with the Bromine evolution process, and connected to the bromine doping chemical stability. Bromine doping, then, is of interest, but must be made time-stable. In fact, stability is a general problem for CNT doping. Therefore, we were interested to see if Cu metallization could increase the stability of doping more generally. To explore this, we decided to test the temperature stability of a doped yarn available from DexMat, listed in Table 1 and S6 and S7. One DexMat pre-doped (proprietary doping) yarn (S6) and the same yarn with Cu electroplating (S7) were tested for $\sigma_e$ at elevated temperatures. Other than the applied Cu plated, S7 was exactly same as S6, and the dopants in the two wires are stable at room temperature. As presented in Figure 5B, S7 showed a small linear dependence of composite resistivity on temperature, while the composite resistivity of S6 increased exponentially upon heating, presumably as a result of the release ("burn-off") of the dopant. The constant $\sigma_e$ of S4 and S5 with time (see Figure 5A) and the linear response of resistivity of S7 with respect to temperature demonstrate that...
FIGURE 5  A, $\sigma_e$ versus time measured for S2 (Brominated yarn), extracted $\sigma_e$ for the CNT yarn in S4 (Brominated yarn with thin Cu plating), and extracted $\sigma_e$ for the CNT yarn in S5 (Brominated yarn with thick Cu plating); B, composite resistivity dependence on temperature of S6 (DexMat doped yarn) and S7 (DexMat doped yarn with Cu plating). The $\sigma_e$ measurement error smaller than the size of the data points in Figure 5A.

the Cu metallization layer can serve as a method of stabilizing CNT yarn dopants. The loss of the bromination effect for un-metallized strands (S2) as well as the loss of dopants for the pre-doped yarns (S6) is presumably due to a two-step process. Considering the brominated yarns, first the bromine must disassociate from the CNT yarn, and then it must diffuse out into the ambient environment. However, we show above that the interphase material present at the CNT/Cu boundary contains significant Br. In addition, both the interphase region and the Cu encapsulation (metallization) serve as diffusion barriers which will slow bromine transport. The lack of rapid diffusion and bromine removal will generate a chemical potential at the interphase/CNT material which will prevent further bromine diffusion through the CNT; thus, preserving the bromine doping. A similar mechanism can be expected for the pre-doped CNT yarns which have been metallized.

3.1 Ampacity measurements

Subsequent to our SEM and $\sigma_e$ measurements, we performed ampacity measurements ($I$-$V$ measurements performed to failure) on bare CNT yarns with and without bromination (S2 and S1, respectively) as well as Cu plated yarns with and without bromination (S5 and S3, respectively), and the results are shown in Figure 6. The brominated bare yarn (S2) was measured just after bromination. We can see that not only does the brominated yarn (S2) have a lower resistivity than the un-brominated yarn (S1), but the limiting current (ampacity) is higher. It can be noticed there is an inflection point when the applied current reaches 1.24 A, shown in Figure 6A, and the $I$-$V$ curve of S2 after this point displays a higher resistance which may be due to a doping-dissociation of Br$_2$ via joule heating. Although S1 and S2 show good values of $\sigma_e$, these two yarns suffer from localized failure. Composites S5 and S3, with and without bromine doping, respectively, had much improved ampacity by virtue of their introduction into a metal-matrix composite as listed in Table 3 and shown in Figure 6B.

The specific electrical conductivity, $\sigma_{em}$, a metric equal to the $\sigma_e$ divided by mass density, was calculated for each sample and these results are listed in Table 3. The Cu-plated composites (S3, S4, and S5) acquire specific electrical conductivities that are comparable to the specific conductivity of Cu, which is 6477 (S•m$^2$•kg$^{-1}$).

According to the rule of mixtures and a parallel resistor model, the composite resistivity is given by

$$\frac{1}{\rho_{total}} = \frac{f_{Cu}}{\rho_{Cu}} + \frac{f_{CNT}}{\rho_{CNT(Cu)}} + \frac{f_{int}}{\rho_{int}}$$

(1)

where $\rho_{total}$ is the average total resistivity, while $\rho_{Cu}$, $\rho_{CNT(Cu)}$, and $\rho_{int}$ are the resistivities of Cu, the CNT after Cu-electrodeposition, and the interface regions, respectively. Here, $f_{Cu}$, $f_{CNT}$, and $f_{int}$ are the fractions of Cu, CNT, and the interface regions, with respect to the total cross sectional area. We note here that it is conceptually useful to give Equation (1) in terms of resistivities. But,
in practice, it is useful to consider the equivalent form of Equation (1) which is in terms of resistance, which makes it clearer how error propagates. Because of the chemical nature of the interphase material, its resistivity can be assumed to be very high, and thus this term effectively drops out of our calculation. Then using $1.723 \times 10^{-8} \text{m} \Omega$ as the room temperature resistivity of Cu,\[26\] we can evaluate the resistivity of the CNT yarns after Cu electro deposition, and the results are given in Table 3. This allows us to explore the effect of metallization on the $\sigma_e$. For example, the as-received yarn (S1) had a $\sigma_e = 3.14 \text{ MS m}^{-1}$, but the $\sigma_e$ of the CNT fraction of S3 (i.e., after Cu electrodeposition) was 2.57 MS m$^{-1}$. The brominated yarn (S2) had an $\sigma_e$ of 7.00 MS m$^{-1}$, while after Cu electrodeposition the $\sigma_e$ estimated for the CNT yarns from composites S4 and S5 were 6.13 and 6.17 MS m$^{-1}$, respectively. These $\sigma_e$ results are excellent for acid-densified, halide-doped yarns,[14,27] and represent an increase in the $\sigma_e$ nearly 2X over the as-received yarns. We anticipate that this process could be used to improve the results recently seen for higher aspect ratio CNTs (which have achieved 8.5 MS m$^{-1}$[14]) as well.

Based on our measurements above, we speculate that here the Cu works as an n-type dopant, that is, an electron-donor, to the CNTs. In addition, we note that the work function of Cu is 4.65 eV,\[28\] and the work function of pristine, bundled CNTs is about 4.8 eV.[29] We believe the work function of the as-received and the brominated CNT yarns are even higher than 4.8 eV because they are both p-type doped. Therefore, we should expect that the Cu plating would reduce the $\sigma_e$ increases due to bromine doping. This is consistent with our measurements above, but the reduction is modest, and a modest price to pay for the observed gain in the time and temperature stability of the doping.

3.2 Calculation of a transfer length

In our analysis, we assumed that the interphase has a low $\sigma_e$. Hence, it is necessary to discuss the current transfer from the Cu through the interphase (dead-layer) to the CNT yarn. An approximate current transfer length from the Cu to the CNT yarn can be determined by equating the resistance of the two paths, one through the Cu sheath, and the other through the interface layer, to the CNT layer, and then back through the interface layer. For an infinitely long wire, the composite should act as two resistors in parallel, one the Cu sheath and the other the CNT layer. In order for that to be approximately true for a wire of a given length, the interlayer resistance should be small compared to both the CNT layer and also the sheath. In our case, the latter condition is more restrictive and thus we need to compare the resistance of the interface layer (transversely) given by $R_{int}$ to that of the Cu sheath, $R_{Cu}$

\[
R_{int} = \frac{\rho_{int} \ast I_{int}}{A_{int}} = \frac{\rho_{int} \ast I_{int}}{2\pi \ast r_{CNT+int} \ast L_{ XF}}
\]

\[
R_{Cu} = \frac{\rho_{Cu} \ast L_{XF}}{\pi \ast (r_T^2 - r_{CNT+int}^2)}
\]

where $R_{int}$ is the resistance of the interphase over the transfer length $L_{XF}$, $R_{Cu}$ is the resistance of Cu over the transfer length $L_{ XF}$, $I_{int}$ is the thickness of the interphase layer which is $\approx 0.8 \mu$m based on SEM analyses, and $\rho_{int}$ and $\rho_{Cu}$ are the resistivities of the interphase and Cu, respectively. We assume the composites are cylindrical for simplicity. Here $r_T$ is the radius of the wire, and $r_{CNT+int}$ is the radius of the cross-sectional area consisting of the CNT and the interphase region. Thus, the area of the cylindrical

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**FIGURE 6** Ampacity measurement for (A) S1 (As-received yarn) and S2 (Brominated yarn); B, S3 (As-received yarn with Cu-plating) and S5 (Brominated yarn with thick Cu-plating)
contact surface of the Cu and interphase material over the transfer length is given by \( A_{\text{int}} = 2\pi r_{\text{CNT+int}} \times L_{XF} \). The transfer length can be found by equating \( R_{\text{int}} \) and \( R_{\text{Cu}} \); thus,

\[
L_{XF} = \sqrt{\frac{\rho_{\text{int}}}{2\rho_{\text{Cu}}}} \times \sqrt{\frac{L_{\text{int}}}{r_{\text{CNT+int}}}} - r_{\text{CNT+int}} \tag{3}
\]

If \( L \gg L_{XF} \), then the current distribution in the wire will approximate that of an infinitely long sample. In our particular case, if we put our known values into Equation (3), and also assign \( \rho_{\text{int}} \) to be \( 10^{-2} \) Ωm (which is a typical value for CuO), \( L_{XF} \) is calculated to be 3 mm. In our experiment, the length of each sample was 9 cm, the gauge length was 3 cm, and the voltage tab to current lead distance was 3 cm, 10X our estimate of \( L_{XF} \).

### 3.3 Mechanical testing

In a final series of experiments, we performed tensile tests for these CNT/Cu composite conductors. Figure 7 shows the mechanical test data for four samples, S2 and S1 (bare yarn with and without bromination) as well as S4 and S5 (brominated yarn with thin and thick Cu electroplates, respectively). It can be seen that bromination has no significant effect on the Young’s modulus (\( E \)) or the UTS of the yarn; thus, the bromination only modifies the electronic properties of the composites/yarns. However, the stress-strain curve for the brominated sample is noisier than the as received sample. The UTS values of the as-received and brominated yarn are similar, 937 and 960 MPa, respectively. These UTS values are much smaller than the values of individual CNTs, but this is not unexpected, because of the weaker bonding forces holding the CNTs within the yarn to one another as compared to the forces holding the CNTs themselves together. The response of S1 and S2 during the first 2.5% of the strain is concave upward due to general fiber straightening. After this, the remainder of the stress-strain curves for S1 and S2 show a linear-elastic behavior with a modulus of 18.2 GPa. The CNT yarns (S1 and S2) break at the end of elastic deformation with very limited plastic deformation. Composite S4 (thick Cu plating) shows a linear elastic behavior, and S5 (thinner Cu plating) initially has the same slope as S4, but is concave downward, with a slope which decreases with increasing deformation. Yarns S4 and S5 have UTS values of 704 and 369 MPa, and Young’s modulus values of 22.8 and 11.6 GPa, respectively. As might be expected, the higher CNT content sample has a higher UTS and \( E \). The maximum elongation of both S4 and S5 is \( \pm 3\% \), similar to the values for S1 and S2 after removing the contribution from yarn straightening. The UTS of S1, S2, S4, and S5 are normalized to their mass densities to obtain the specific UTS values listed in Table 4, and all of the composites/yarns have a much higher specific UTS than Cu, which is 24.54 (KN*m kg \(^{-1}\)).[31] In addition, the stress-strain curves of S4 and S5 do not show any fiber pull-out behavior, which means that we have good bonding between the CNT yarns and the Cu matrix.[32]

### 4 CONCLUSIONS

Because of their merits in terms of high charge carrier mobility, high strength, and low density, carbon nanotubes (CNTs) are an ideal materials with which to begin to develop strong, light-weight, composite conductors. We set out to do this by doping and then metallizing a set of high performance CNT yarns which had, in their as-received state, average electrical conductivities of 3.14 MS m\(^{-1}\) and mass densities of 1.32 g cm\(^{-3}\). We doped these yarns with...
bromine, and were able to reach an $\sigma_e$ of 7.00 MS m$^{-1}$, which is very good for CNT conductivity. We interpreted this result in terms of an electron transfer from the CNT to the halide/p-type-dopant. However, this increase in $\sigma_e$ was not stable with time, with significant decreases were seen over a 2 month period. In order to increase the time and temperature stability of this doping, we plated a Cu layer onto the doped yarn using a continuous reel-to-reel process with an acid-aqueous solution. After metallization, some electrons transfer occurred from the Cu to the CNT, reducing the conductivity, although the effect was modest. Our analysis gives a value of 6.15 MS m$^{-1}$ for the brominated yarn after Cu-metallization which is still quite good for acid-densified, doped CNT yarns. We then measured the $\sigma_e$ of the doped and Cu-plated CNT yarn left in ambient conditions (at room temperature, in air) at specified intervals over a time span of more than 2 months, and found the $\sigma_e$ improvement to be constant. The Cu-electrodeposited composites showed a Cu-CNT interphase which had a thickness of $\pm0.8 \mu$m (the thickness varied slightly depending on the weaving structure of the fibers within the yarns). Either the interphase layer or the Cu itself appeared to act as barrier to prevent the diffusion of dopants. The $\sigma_e$ of Pre-doped CNT/metallized yarns were then measured as a function of temperature and these results were compared to pre-doped but unmetallized yarns, and it was seen that metallization also increased the temperature stability of the doping. Thus, we conclude that metallization can help stabilize doped CNT yarns with respect to time and temperature. Although placing Cu in contact with CNTs may serve as a compensational dopant for the p-type doped yarns, allowing some charge carrier recombination, the brominated yarns after Cu-electrodeposition still shows an $\sigma_e$ of 6.15 MS m$^{-1}$ within the CNT yarns. We anticipate that the brominization+metallization process use here could be used to improve the results for higher aspect ratio CNTs as well. Finally, we report that tensile tests on Cu/CNT composites showed tensile strengths as high as 700 MPa, a Young’s modulus of 22.8 GPa, and a specific tensile strength as high as 146 kN*m kg$^{-1}$ (which is about 6X that of Cu). The final CNT-Cu composites show specific electrical conductivities comparable to that of Cu but with a much higher specific tensile strength.

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** CONFLICT OF INTEREST **

The authors declare that they have no known competing financial interests or personal relationships that have influenced the work reported in this paper.

** DATA AVAILABILITY STATEMENT **

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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**TABLE 4 Mechanical test results**

| Composite conductor | Tensile strength [MPa] | Young’s modulus [GPa] | Specific tensile strength [KN*m kg$^{-1}$] | Stiffness [N m$^{-1}$] |
|---------------------|------------------------|-----------------------|-------------------------------------------|------------------------|
| S1 (As received yarn)| 938                    | 18.6                  | 713±3.9%                                   | 2570                   |
| S2 (Brominated yarn)| 960                    | 17.8                  | 620±2.0%                                   | 2400                   |
| S4 (Brominated, thin Cu) | 704                  | 22.8                  | 146±8.6%                                   | 3980                   |
| S5 (Brominated, thick Cu) | 370                | 11.6                  | 58.5±1.8%                                  | 4870                   |

* a Errors are estimated from the area variations given in Table 2.
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