Conductivity scaling with bundle length and diameter in single walled carbon nanotube networks

David Hecht, Liangbing Hu, and George Grüner[a)]
Department of Physics and Astronomy, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095

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Transparent single walled carbon nanotube (SWNT) networks were printed on plastic substrates. Nanotubes in the network form small bundles, and the authors evaluated the dc conductivity (σ_{dc}) as a function of the average bundle length (L_{av}) in the network. They find σ_{dc} to vary as $\sigma_{dc} \sim L_{av}^{1.46}$ for bundles of the same diameter and give a qualitative argument for why this agrees with a model where the resistance between SWNT bundles dominates the overall network resistance.
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Single walled carbon nanotube (SWNT) networks are emerging as an interesting material with significant application potential in the area of flexible transparent electrodes. SWNT electrodes can be formed by several room temperature, solution based processes including spray coating[1] and deposition through a filter.[2] Recently, a printing method has shown that SWNT networks on a plastic substrate rivals indium tin oxide (ITO) in the important parameters of optical transparency and sheet resistance.[3] Furthermore, SWNT networks have been demonstrated to function with performance comparable to ITO for a variety of applications including electrodes for solar cells,[4] smart windows,[5] sensors,[6] and transparent transistors.[7] However, further improvement in the conductivity of these SWNT networks is needed to make them a truly viable alternative to ITO.

There have been several reports on the conductivity of SWNT networks, with values ranging from 400 (Ref. 8) to 6600 S/cm.[9] The discrepancy in these values arises due to the many factors that can affect the conductivity of SWNT networks, including the doping level of the semiconducting tubes, sample purity, and the metallic to semiconducting volume fraction. In addition, the geometry of the bundles that comprise the network is expected to have a substantial impact on the network conductivity. In the present study, the conductivity of SWNT networks is measured as a function of the average length (L_{av}) of the SWNT bundles within the network. The results will be discussed in terms of a model where the SWNT bundle-bundle resistance dominates the total network resistance.

A SWNT network is comprised of two distinct sources of resistance: (1) the resistance along the SWNT itself (R_{NT}) and (2) the resistance due to the tube to tube junction (R_{jct}). Networks can therefore be broadly divided into two classes; one where $R_{NT} \gg R_{jct}$ and one where $R_{jct} \gg R_{NT}$ (the case where $R_{jct} \sim R_{NT}$ is more complex and not discussed here). In the former case, the conductivity of the network should be independent of the length of the tube, for films that are well above the percolation threshold. To demonstrate this, imagine taking a network of SWNTs and cutting each SWNT in half. If the junction resistance is negligible, this would not increase the resistance of the sample but would decrease the average SWNT length. One could repeat this process to show that the sample resistance would be independent of the SWNT length. If the junction resistance dominates the total network resistance, however, the conductivity of the networks will be higher for networks comprised of longer tubes, because there will be fewer tube-tube junctions across the sample. In fact, simulations on networks of conducting sticks near percolation have shown that the conductivity of the network goes as a power law of the stick length as $\sigma \sim L^{2.48}$ (Ref. 10) in a model where the stick to stick resistance dominates the network resistance. The exponent 2.48 is expected to be an upper bound, as that study was done for networks near the percolation regime, where percolation effects also contribute to the conductivity increase. Therefore, we expect the conductivity to go as a power law in length with an exponent between 0 (when junction resistance is negligible) and 2.48 (when the junction resistance dominates the network resistance).

Previous measurements have shown that SWNT networks fall into the latter category, where the resistance is dominated by the junctions between bundles.[11] Measurements on crossed SWNTs show that the junction resistance between SWNTs is about 200–400 kΩ for a metal/metal or semiconducting/semiconducting SWNT junction, and about two orders of magnitude higher for a metal/semiconducting junction (at low bias voltage).[12] Since we use small bundles of tubes consisting of a mixture of semiconducting and metallic tubes, we expect metal/metal, metal/semiconducting, and semiconducting/semiconducting junctions to contribute to the junction resistance. Measurements of the resistance along a single SWNT show that the resistance has a minimum of about 6–7 kΩ for tubes shorter than 500 nm (ballistic regime); for longer tubes, the resistance scales with length at about 6 kΩ/μm.[13] The maximum SWNT channel resistance expected in our study comes from the longest tubes of 3–4 μm, which has been measured to be about 30–60 kΩ for palladium contacted individual SWNTs, and should be even lower in our case since we are using small bundles.[14] Therefore, our SWNT networks are in a regime where the junction resistance between bundles is about one to two orders of magnitude higher than the resistance along the bundle, such that the junctions dominate the overall network resistance. In this regime, one expects the network conductivity to increase as a power law with increasing nanotube length, as each charge carrier has to cross fewer and

[a)]Electronic mail: ggruner@ucla.edu

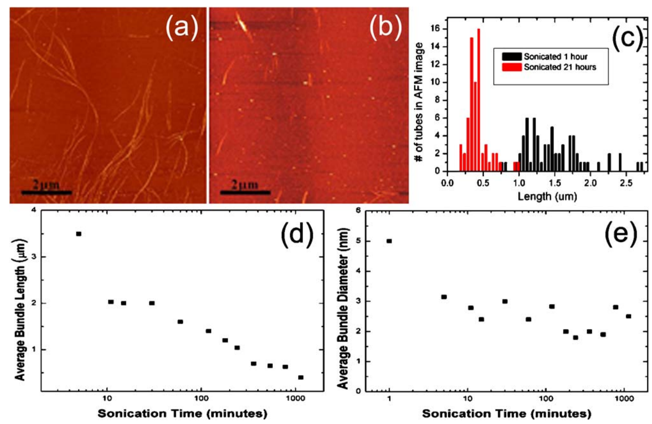

FIG. 1. (Color online) Effects of sonication on SWNT bundle length and diameter. [(a) and (b)] AFM image of SWNTs absorbed on a silicon wafer after (a) 1 h and (b) 21 h of sonication time. (c) Histogram of bundle length distribution taken from several AFM images for 1 h (black) and 21 h (red) of sonication. Plot of the (d) average bundle diameter and (e) average bundle length for various sonication times measured from AFM images.

fewer junctions to traverse the sample. To test this hypothesis, SWNT networks of various average tube lengths were fabricated.

Measurements were made on carbon nanotubes made from two distinct sources: (1) arc discharge (P3, purchased from Carbon Solutions) and (2) laser ablation. The results were qualitatively similar for both SWNT sources; only the results from the laser ablation tubes will be shown here. The laser ablated tubes were purified using a nitric acid reflux treatment, which leaves the semiconducting nanotubes doped to some extent.[9] The nanotubes were dispersed into a 1% solution of sodium dodecyl sulfate (1 mg/ml) by a probe sonicator. It has been shown that sonication of carbon nanotubes in an appropriate solvent can cut the nanotubes into shorter segments.[15] In order to cut the as received nanotubes into tubes of smaller lengths, the dispersions were sonicated for various lengths of times, from 1 min to 21 h, using a probe sonicator. At various times, an aliquot of the solution was removed from the dispersion and centrifuged for 1 h at 16 000 rcf (rcf denotes relative centrifugal force). The supernatant was carefully decanted and used for two purposes. First, a drop of solution was placed on a silicon wafer so that tubes could absorb to the surface of the wafer for atomic force microscopy (AFM) imaging. Second, the same solution was used for making transparent films using the method outlined by Zhou *et al.*[3] Figures 1(a) and 1(b) show typical AFM images of the laser tubes at various sonication times (1 and 21 h); using several of these images for each sonication time, one can measure the distribution of tube lengths in the network (Fig. 1(c)), as well as the average bundle length and diameter (D_{av}) for each sonication time [Figs. 1(d) and 1(e)]. To calculate a bundle length, only the end to end distance was measured; any tube length in bends and curls was not included in the length measurement. Noticeable is the fact that both L_{av} and D_{av} decrease with longer sonication times, as the sonication power both cuts tubes lengthwise and separates bundles that are held together through van der Waals interactions. Figures 1(d) and 1(e) show that the length of the tubes decreases exponentially with sonication time from 4 μm initially, to 0.4 μm after about 21 h of sonication, and that the diameter of the bundles decreases sharply initially from 5 to 3 nm in the first 5 min of sonication, and then

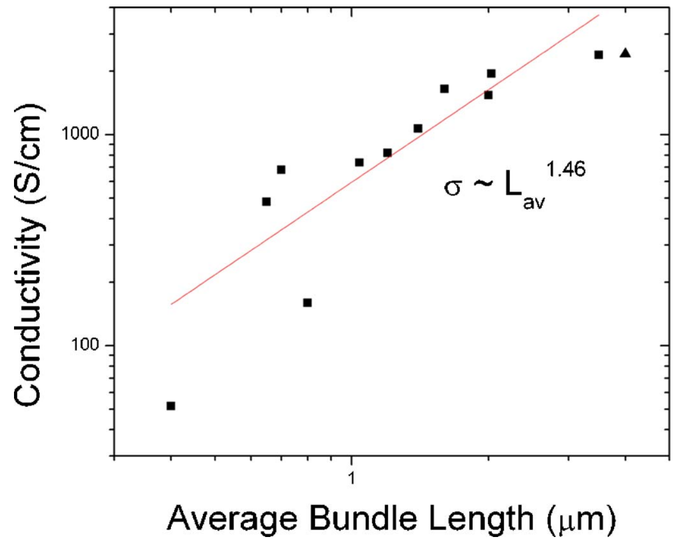

FIG. 2. (Color online) DC conductivity of SWNT networks vs average bundle length in the network. Data are fit to a power law, $\sigma_{\mathrm{dc}} \sim L_{\mathrm{av}}^{\alpha}$ with $\alpha = 1.46$. Data for 4 μm length tube (triangle) is excluded from the fit because of the larger bundle diameter for that data point.

remains constant between 2 and 3 nm after that.

At each sonication time, the aliquot of solution that was imaged was also used to make SWNT network films by the method outlined by Zhou *et al.*[3] First, the aliquots of centrifuged SWNT solution taken after various sonication times were diluted and deposited on an alumina filter using vacuum filtration. Then, thin SWNT films were printed from the filter to a polyethylene terephthalate (PET) plastic substrate using a polydimethylsiloxane (PDMS) stamping method. The transmission (at 550 nm) through the SWNT films on PET was measured using a Beckman Coulter DU 640 spectrophotometer, with a blank piece of PET as background; the sheet resistance of the SWNT films was measured using a two probe measurement. These two parameters of transparency (T) and sheet resistance (R_s) are related to the dc conductivity and optical conductivity (σ_{op}) of the films using[16]

$$T = \left(1 + \frac{1}{2R_S}\sqrt{\frac{\mu_0}{\varepsilon_0}}\frac{\sigma_{\mathrm{op}}}{\sigma_{\mathrm{dc}}}\right)^{-2}$$

$$= \left(1 + \frac{188(\Omega)}{R_S}\frac{200(\mathrm{S/cm})}{\sigma_{\mathrm{dc}}}\right)^{-2}. \quad (1)$$

Here, the free space permeability $(\mu_0)=4\pi\times 10^{-7}$ N A^{-2} and the free space permittivity $(\varepsilon_0)=8.854\times 10^{-12}$ C^2 N^{-1} m^{-2}. In calculating σ_{dc}, we use the previously measured value of 200 S/cm for the optical conductivity of SWNT networks at 550 nm.[17] This method of calculating σ_{dc} of the SWNT films using the transmission and sheet resistance yields σ_{dc} within 10% of that given by measurements of the sheet resistance and film thickness.[3] All films measured were between 78% and 82% transparent at 550 nm.

Figure 2 shows a plot of σ_{dc} of the films versus the average bundle length in the network. It is apparent that there is an increase in network conductivity as the average bundle length increases, because longer tubes lead to fewer tube-tube junctions on average to traverse the sample. This is illustrated in Fig. 3(a). Assuming that the conductivity has a power law dependence on the length of the bundles (as a functional form suggested by the theory in certain limits), we

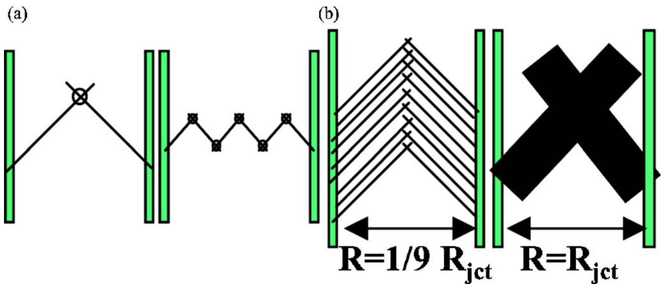

FIG. 3. (Color online) Qualitative argument for the dependence of the dc conductivity of SWNT networks on the average bundle length and diameter. (a) Longer tubes lead to fewer junctions to cross the surface, which leads to higher conductivity. NT-NT junctions are circled. (b) Larger bundles lead to lower conductivity as $\sigma \sim D_{av}^{-2}$ for stiff bundles where R_{jct} is independent of the bundle diameter.

expect $\sigma_{dc} \sim L_{av}^{\alpha}$ with the exponent between 0 and 2.48 as discussed previously. However, this is only meaningful for samples where the bundle diameter does not vary concurrently with the average bundle length, because the diameter of the bundle should also have an effect on the sample conductivity. The reason for this can be seen in Fig. 3(b). Imagine two separate samples: sample 1 consists of a junction between two bundles of x tubes each, and sample 2 consists of x single tube junctions. Assume that the resistance of the sample is dominated by the resistance of the junction. Furthermore, assume that the bundles are perfectly rigid, such that the contact area between bundles is independent of the bundle diameter (this assumption will be modified further in the discussion); this assumption leads to R_{jct} being independent of the bundle diameter, as R_{jct} is expected to be a function of the overlap area between bundles. Using these assumptions, the resistance of the sample is simply given by the number of junctions. Therefore, since sample 1 has 1 junction, the resistance of the sample is R_{JCT}, and since sample 2 has x junctions in parallel, the resistance of the sample is $(1/x)R_{jct}$. Since both samples have the same number of SWNTs (same volume of material), sample 2 will have x times the current density of sample 1 and will therefore have x times higher conductivity. Furthermore, the bundle diameter varies as the square root of the number of tubes in the bundle, such that $D_{av} \sim \sqrt{x}$. This analysis leads to $R_{sq} \sim x \sim D_{av}^2$ or $\sigma \sim 1/D_{av}^2$. However, this was under the assumption that the bundles were perfectly rigid, such that the contact area between bundles was independent of the bundle diameter. However, it is likely that SWNT bundles deform at least slightly,[18] so that there is more contact area between larger bundles. Therefore, R_{jct} would, in fact, be lower for bundles with larger diameter, as there would be more contact area between bundles; this is like having several R_{jct} in parallel. Therefore, one expects that the conductivity of a SWNT network will go like $\sigma \sim 1/D_{av}^{\beta}$ with $\beta = 2$ being an upper limit to the exponent; this implies that better SWNT dispersion will lead to networks with higher conductivity.

Due to the fact that the conductivity of the network is expected to depend on the average bundle diameter, the data point in Fig. 2 obtained for the 1 min sonication time was excluded in our fit to $\sigma \sim L_{av}^{\alpha}$, as the bundles in that sample clearly had a larger diameter than in the rest of the samples (data point represented by a triangle in Fig. 2). Fitting the data to the remaining points (squares in Fig. 2) yielded $\sigma \sim L_{av}^{1.46}$. Because we could not generate samples where the length remained constant, but the bundle diameter changed, we could not determine β; however, those studies are currently underway.

Given that the conductivity varies like $L_{av}^{1.46}$, one expects to see improvement in the conductivity of SWNT networks as the length of tubes continues to increase. However, when the tubes in the network approach 20–30 μm, the resistance along the tube itself becomes comparable to the resistance of the junctions;[13] further increase in the SWNT tube length will have limited impact on the conductivity of the networks. Assuming that the power law dependence of $L_{av}^{1.46}$ holds true up to this crossover region where the tubes ~25 μm lead to a predicted network conductivity of ~30 000 S/cm or 80% transmission at 550 nm with 10 Ω/sq. This would compare favorably with ITO on plastics, which currently can be made at 60–250 Ω/sq and 80% transmission at 550 nm.[19] Further increases in conductivity in the SWNT networks may be possible by doping, purification of the tubes, or enrichment of the metallic fraction.

In conclusion, we fabricated SWNT networks where the geometry of the bundles in the network was varied. We find that the conductivity of these networks varied as a power law in the average bundle length, with an exponent of 1.46, and give qualitative arguments for why the conductivity should vary as $D_{av}^{-\beta}$ where β is between 0 and 2. As groups continue to push the length of grown SWNT tubes, the conductivity of these networks will continue to improve and push the application potential of this material.

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