Long Carbon Nanotubes Functionalized with DNA and Implications for Spintronics

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ABSTRACT: Helical molecules such as DNA have recently been found to behave as an efficient source and detector of spin-polarized charge carriers. This phenomenon, often dubbed as chirality-induced spin selectivity or CISS, could be used to significantly improve the performance of spintronic devices, which utilize carrier spins (rather than charge) to realize electronic and sensing functions. Recently, it has been reported that carbon nanotubes, helically wrapped with DNA, can also act as an efficient source and detector of spin-polarized carriers, by virtue of spin−orbit coupling originating from the helical potential. It has been postulated that spin polarization should increase with the length of the wrapped tubes. However, in literature, most fabrication processes yield tubes with submicron lengths, which can produce ~70% spin polarization. In an effort to enhance this effect further, here, we report a fabrication process that can yield DNA-wrapped nanotubes of length ~1–4 microns. Detailed characterization of these devices, using atomic force microscopy, Raman, UV−vis, and temperature-dependent transport, has been presented. Initial transport measurements indicate the presence of strong magnetoresistance in these tubes, which could be attributed to spin-dependent effects. Systematic fabrication of long DNA-wrapped nanotubes, which has hitherto not been reported, is expected to enable further investigation into the spin-dependent properties of these ultimate one-dimensional nanoscale hybrids and may have a significant impact on nanoscale spintronics.

1. INTRODUCTION

Carbon nanotubes (CNTs), rolled up cylindrical forms of two-dimensional hexagonal lattice of carbon atoms (or graphene), have been explored extensively over the last few decades. The carbon atoms in CNTs are sp² hybridized, with strong carbon−carbon σ bonds and available pₓ orbitals. Such a chemical structure leads to excellent mechanical, thermal, electronic, and sensing properties, some of which are already finding commercial applications. At present, significant effort is being spent on realizing future computing technologies using CNTs, via conventional charge-based electronics or emerging spin-based electronics (or spintronics).

One of the major disadvantages of CNTs, however, has been their poor solubility in common aqueous and organic solvents. As-grown nanotubes often take bundled form because of intertube van der Waal’s interaction, and for device applications it is important to have them dispersed. To address this, various types of chemical functionalization techniques have been developed. Functionalization can be performed primarily in two different ways, such as (a) covalent functionalization, which while being chemically stable, adversely affects the intrinsic properties (such as electrical conductivity, toughness, etc.) of the nanotubes by inflicting irreversible structural damage and (b) noncovalent functionalization, which keeps the inherent properties of the nanotubes intact but are comparatively less stable. Chemical functionalizations not only disperse the nanotubes but they often allow separation of tubes based on their electronic properties (semiconducting vs metallic) and also form the basis of a wide variety of electrochemical sensors, by virtue of the attached chemical moieties.

For the purpose of device electronics, noncovalent functionalization is more desirable because it minimally affects the intrinsic electronic properties of the tubes. One simple and efficient approach is functionalization using single-stranded DNA, which has been investigated extensively in the past. The DNA−CNT binding energy is higher than the CNT−CNT binding energy, which facilitates tube separation. The DNA−CNT interaction is mediated by (a) π-stacking interaction between the DNA bases and the pₓ orbitals of the nanotube carbon atoms and (b) electrostatic interaction between nanotube and sugar-phosphate backbone. The DNA strands, due to their intrinsic helicity, tend to wrap the nanotubes in a helical fashion. Such helically wrapped nanotubes have been used for diverse applications in recent years.
Very recently, such helically wrapped nanotubes have found a novel application in the area of spintronics.\textsuperscript{20–23} By definition, spintronics is the subfield of electronics where the goal is to use the spin degree of freedom of charge carriers to realize various sensing and computing devices.\textsuperscript{24} Commonly, ferromagnetic contacts (such as Ni, Co, Fe, and their alloys) are used to generate and detect spin-polarized carriers and are often referred to as “spin filters.”\textsuperscript{25} Recently, it has been discovered that chiral molecules such as DNA can also perform as a spin filter and often with better efficiency than the transition-metal ferromagnets mentioned above.\textsuperscript{26} This phenomenon is commonly referred to as the “chirality-induced spin selectivity” or CISS effect.\textsuperscript{26} Recent theories and experiments have shown that CNTs, helically wrapped with single-stranded DNA, can also play the same role.\textsuperscript{26–28} This opens up a completely new application area for DNA–CNT functionalization chemistry, which has been well developed over the past decade.

In case of the CISS effect, charge carriers become spin-polarized via the spin–orbit interaction induced by the helical potential.\textsuperscript{29} It has been found that spin polarization increases with increasing base-pair length,\textsuperscript{27} presumably because the carriers experience prolonged interaction during their transit through longer chiral systems. By the same token, longer nanotubes, helically wrapped with DNA is expected to produce higher degree of spin polarization. Recent experiments performed on 750 nm long tubes resulted in 70−80% spin polarization.\textsuperscript{28} Because overall efficiency of spintronic devices depends critically on spin-filtering efficiency,\textsuperscript{29} ideally 100% spin polarization is desirable, which could be obtained from longer nanotubes with helical functionalizations. However, most earlier studies on CNT–DNA functionalization (reviewed below) resulted in short tubes (typically less than 1 μm) because of fabrication constraints. Motivated by this, here, we report fabrication of isolated and long (∼1−4 μm) nanotubes, helically wrapped with DNA strands. The fabrication process is applicable for both metallic and semiconducting nanotubes. Functionalized nanotubes have been characterized in detail by atomic force microscopy (AFM), optical absorption experiments, Raman spectroscopy and temperature-dependent electrical transport. Preliminary magnetotransport data has also been presented, which suggests the presence of spin filtering. A detailed study of spin polarization as a function of length is however beyond the scope of this paper and will be reported in a future work.

This paper is organized as follows. In the next section, we briefly review prior work on nanotubes functionalized by DNA, with focus on final tube length. In Section 3, we describe the fabrication process. Results and discussions are presented in Section 4. We conclude in Section 5 with a brief summary and potential implications of this work.

2. PRIOR WORK

Nanotube dispersion can be achieved via functionalizing CNTs by a wide range of polymers.\textsuperscript{12,13,25} Here, however, we will focus on single-stranded DNA because in most cases they wrap the tubes helically\textsuperscript{15,16,30,31} and the composite hybrid has been found to be a promising spin filter system.\textsuperscript{20,21} Typically, nanotube powder is mixed with excess DNA solution. Next, ultrasonication is used to disintegrate the nanotube bundle, which allows the DNA strands to wrap with the tubes. This step also determines the length of the dispersed (and helically wrapped) nanotubes,\textsuperscript{22} which is a critical aspect for spin filter applications as described above. Finally, the mixture is centrifuged, which results in precipitation of unfunctionalized tubes and other impurities. Helically wrapped nanotubes are dispersed in the supernatant solution, which is decanted for further processing.

Reference 15 reported CNT wrapping by various lengths (60-, 30-, 21-, and 15-mer) of poly-T strands, among which T30 produced the highest yield. Typical nanotube length, based on AFM, is ∼50−1000 nm. Reference 16 used d(GT)ₙ (n = 10−45) to isolate SW-CNTs, and length distribution of ∼50−500 nm was observed. In particular, d(GT)ₙ resulted in an average tube length of ∼500 nm.\textsuperscript{32} Reference 34 used long genomic ssDNA (∼3796 bases) with random sequence to disperse CNTs. The average length was found to be ∼700 nm, and in a few instances, 2 μm long nanotubes were observed. Longer tube length was attributed to longer DNA strands and short sonication time (∼10−20 min). However, because of the short sonication period, few nanotube bundles remained in the solution (not well dispersed), which is consistent with other studies.\textsuperscript{25} Natural DNA has been used by several other groups as well.\textsuperscript{35–37} Reference 37 used ∼10 000 base-pair long DNA, which is expected to shorten after sonication. The reported average final nanotube length was ∼260 nm.\textsuperscript{38} References 38 and 39 studied the effect of DNA sequence length on helical wrapping and separation of nanotubes. Short DNA strands, such as d(GT)₂ and d(AC)₃, were found to disperse CNT's more efficiently than the longer ones (d(GT)ₙ and d(AC)ₙ, n = 4, 10, 20, 40). Reference 40 was able to disperse nanotubes by double-stranded DNA. Typical DNA length was ∼100−300 base pairs, and from the AFM data, average nanotube length was around few 100 nm. Reference 41 reported loosening of DNA wrapping as strand length is increased.

3. FABRICATION

The key aspects that determine the length of the final wrapped nanotubes are (i) length of DNA strand because it is expected that long base-pair DNA will wrap longer tube segments and lead to longer wrapped nanotubes and (ii) ultrasonication parameters such as power and duration.\textsuperscript{16} In this work, we focus on d(GT)ₙ strands because they are known to produce efficient functionalization as well as exhibit spin filtering. We report data on d(GT)₂₀₀ which systematically produces nanotubes with length ∼1−4 μm, significantly longer than those reported in the current literature (<1 μm). We varied the ultrasonication duration to maximize the length of the wrapped tubes. We compared our results with shorter d(GT)₁₅ strands and found that longer strands consistently produce efficient dispersion, without sacrificing the length of the tube.

For fabrication of DNA-wrapped long nanotubes, we use d(GT)₂₀₀ strands (Integrated DNA Technologies). First, 20 nmol of DNA oligo is mixed with nuclease-free water and buffer to produce 1 mg/mL ssDNA solution. Next, 0.7 mg of HiPco SW (single-wall)-CNTs (diameter ranging from 0.7 to 1.2 nm, NanoIntegris Inc.) is mixed with this solution, and the mixture was ultrasonicated (Sonics, VC130 PB) for 90 min at a power level of 7 W in an ice-water bath. After sonication, the mixture is centrifuged at 14 000 rpm for 60 min, which precipitates undispersed SW-CNTs at the bottom. The top part of the mixture was collected for further experiments.

A small part of the decanted supernatant solution is drop cast on top of SiO₂ substrate for a few minutes, followed by thorough rinsing with deionized (DI) water and drying under ambient conditions. These specimens are used for AFM.
(Dimension Edge) studies. AFM observations described below suggest that most of the bundled CNTs are converted into individual wrapped tubes. The minimum length of ssDNA–CNTs at this stage is 1 μm and some are as long as 4 μm. For electrical transport measurements, a small amount of ssDNA–CNT supernatant solution was drop cast on prepatterned Au and Ni contacts for 15 min. Next, the substrates are thoroughly rinsed with DI water and vacuum annealed (200 °C for 30 min). Vacuum annealing improves the electrical contacts between the electrodes and ssDNA–CNTs and improves the reproducibility of charge transport measurements. Contact thickness is ∼100 nm (Figure S6, Supporting Information), and they were photolithographically patterned on top of SiO$_2$ (500 nm)/Si wafer.

Figure 1. (a–f) AFM images of dispersed nanotubes wrapped with d(GT)$_{200}$ and d(GT)$_{15}$. Ultrasonication times are indicated in each image. (g,h) Both strands result in similar wrapping pitch.
4. RESULTS AND DISCUSSION

Figure 1a shows d(GT)200 wrapped nanotubes dispersed on SiO2 substrate. Figure 1b-d shows representative images of tubes with length ∼1-4 μm. For the purpose of comparison, Figure 1e shows wrapping using d(GT)15 under the same fabrication condition as above. In this case, however, tubes are <1 μm, which is consistent with previously published data cited above. Additional AFM image corresponding to this case is shown in Figure S1a (Supporting Information). Clearly, length of the strands plays a role in determining the final length of the wrapped tubes. To check if reducing the sonication time using CNT [or, sodium dodecyl sulfate (SDS) solution was cast on a quartz substrate and naturally dried. We observed, with d(GT)200 resulting in more than double the final length of the nanotubes. Clear dispersion by the DNA strands. Compared with SDS, indicating more effective increase in the tube stiffness in the radial direction, resulting in higher wavenumbers. This feature confirms tight physical wrapping of nanotubes by the DNA strands.

After DNA wrapping, RBM peaks tend to get narrower, as a result of dispersion and nanotube isolation (Figure 3a). For example, d(GT)15 and d(GT)200 lead to fwhm (main peak) of ∼11.94 and 12.15 cm⁻¹, respectively. DNA wrapping also leads to fewer peaks compared with the bundle because of fewer population of nanotubes in the sample and diameter selectivity of the wrapping process. Interestingly, the peak positions are shifted slightly (∼4 cm⁻¹) toward higher wavenumbers. DNA wrapping tends to constrain the radial vibration of the carbon atoms, leading to an effective increase in the tube stiffness in the radial direction, resulting in higher wavenumbers. This feature confirms tight physical wrapping of nanotubes by the DNA strands.

Comparing all of the three reagents used for dispersion, it appears that d(GT)15 and d(GT)200 are approximately equally effective in terms of wrapping compactness. On the other hand, dispersion using SDS does not appear to be as effective as the DNA strands because the RBM band closely resembles the bundled CNT.

Figure 3b shows the TM mode (or G band) for nanotube bundle and after functionalization with three different reagents. The TM mode has two prominent peaks: G', which occurs around 1580 cm⁻¹ and G”, which occurs at lower wavenumbers (∼1525 cm⁻¹). The G’ peak originates from the longitudinal vibrations of carbon atoms along the tube axis, whereas G” is due to the circumferential vibrations. The
force constant of C–C bonds is larger along the longitudinal direction compared with the tangential direction, which explains the difference between the frequencies of these two bands. After DNA functionalization, circumferential vibration gets quenched because of tight wrapping with DNA strands, which results in weaker G− peaks, as can be seen clearly from Figure 3b. Overall, as expected, the G band gets narrower after dispersion, compared with the bundle. For example, the G+ peak has a fwhm of 41.83 cm−1 for bundled tubes, which reduces to 17.9 cm−1 for d(GT)200 wrapping and 22.12 cm−1 for d(GT)15 wrapping. Wrapping with SDS reduced the fwhm to 35.34 cm−1, which is not as pronounced as the DNA strands mentioned above. Functionalization also causes charge transfer between the tube and DNA strands, resulting in slight upshift in the peak locations.42 For the DNA strands, this shift is ∼10 cm−1, whereas for SDS, it is only ∼3 cm−1. This reconfirms tight physical wrapping of the nanotubes by DNA strands.

Figure S5 (Supporting Information) shows summary (average and standard deviation) of Raman data collected from multiple (∼5) scans and multiple samples. The qualitative features described above represent the general behavior exhibited by these specimens.

The G+ peak can be fitted with a Lorentzian, whereas G− peak requires a broad Breit–Wigner–Fano lineshape and two Lorentzians, as shown in the inset of Figure 3b. This feature is a signature of metallic nanotubes and arises due to coupling of phonons with the continuum of electronic states near the Fermi level of metallic nanotubes.44 Semiconducting tubes, on the other hand, do not exhibit such a feature, and in that case, both G+ and G− peaks can be fitted with Lorentzians.

Figure 4 shows the two-terminal temperature-dependent I–V characteristics for d(GT)200 wrapped nanotubes. Contact resistances of such devices have been characterized in our prior work45 and have been found to be negligible. This could be attributed to the annealing step described above, and a similar effect has been reported by other groups as well.46 For this study, the channel length is set to ∼750 nm, as seen in Figure 4 insets and Figure S6 (Supporting Information). Multiple tubes could be present in between the contacts but only very few are electrically connected with both contacts (shown by arrows). Bottom-right inset shows only one tube connected between the contacts.

DNA molecules are known to exhibit large-band gap semiconducting behavior, even at room temperature.48,49 Typically, in the low bias range, DNA strands exhibit very low conductance and essentially behave as an insulator.48,49 This is in contrast with the data observed in Figure 4, which shows low but measurable conductance in this range. This indicates that the primary transport channel is the nanotube
Figure 5. Typical I–V characteristics at +1.2 and −1.2 T, showing the presence of MR at 9 (a) and 21 K (b). (Insets) Variation of device resistance as a function of bias.

and not the DNA strands on the periphery. This is consistent with the device geometry because direct one-step coherent tunneling through 750 nm wide potential barrier (due to DNA strands) is extremely unlikely. Also, in such a case, current should be almost independent of temperature, which we do not observe. Incoherent thermally activated hopping could provide another transport mechanism through the DNA strands, but this should be ineffective at low temperatures, and even at higher temperatures DNA strands still behave as insulators. Further, in case of DNA, the conductance gap at low bias tends to increase with temperature, which is qualitatively different from what we observe. Thus, in our case, carrier transport appears to be taking place via the nanotubes. The role of DNA functionalization is to induce an inversion-asymmetric helical potential on the charge carriers, which is necessary for subsequent device fabrication.

Because nanotubes are the primary transport channels, the I–V scans are highly reproducible with negligible deviations between multiple scans taken under the same conditions. This is shown in Figure S7 (Supporting Information). We note that while ssDNA–single-walled carbon nanotube (SWCNT) hybrids are unstable above 80 °C in aqueous solutions, the critical temperature for these hybrids adsorbed on SiO2 is much higher. Using a binding energy value of 0.7 eV for ssDNA–SWCNT hybrids from this study, we can estimate the critical temperature for instability on SiO2 substrate, which turns out to be approximately few 1000 K. This value is significantly larger than our annealing temperature (200 °C or 473 K), and hence, no DNA unwrapping is expected. We have examined the nanotubes by AFM after annealing (Figure S10, Supporting Information) and the same helical wrapping pattern was observed, indicating that the DNA molecules were not destroyed as a result of annealing.

Figure 5 shows I–V characteristics at 9 and 21 K for two different magnetic field values +1.2 and −1.2 T. Magnetic field is applied in-plane and is sufficient to saturate the magnetic Ni contact, which has a coercive field of ~100 G. A clear splitting in the I–V curve has been observed, which indicates the presence of a magnetoresistance (MR) effect in these devices. The insets in Figure 5 show the resistance (R = dV/dI) as a function of bias (V), computed by numerical differentiation of the I–V characteristics. At a given bias, a significant split in the resistances has been observed, especially in ±0.1 V range. The MR effect gradually disappears as the bias is increased. Also, at higher temperatures (such as 70 K), the MR effect is not present (Figure S8, Supporting Information).

As indicated above, the I–V scans are highly reproducible and the observed splitting cannot be attributed to statistical variations. As an example, Figure S9 shows multiple scans at each magnetic field, the average value, and the standard deviations. The magnetic field-dependent splitting is still observed.

The magnitude of the MR value (defined as R(1.2 T) – R(−1.2 T)/R(−1.2 T)) is significant ~90% at 0.1 V and 9 K and cannot be explained by AMR (anisotropic MR) of Ni contact, which is typically ~1%. Also, as the temperature-dependent I–Vs indicate, the series resistance of the metallic contacts does not play any perceptible role in the overall device resistance. Such a large MR signal is indicative of spin-dependent transmission at the Ni contact, which acts as a spin detector. These data suggest that d(GT)200 strands are capable of spin filtering, consistent with existing literature. Using Julliere model and assuming 33% spin polarization for Ni, we estimate a typical spin polarization value of 79% at −0.1 V and 21 K. Because d(GT)200 functionalization creates longer tubes, it is possible to perform a systematic length-dependent study of spin polarization using these tubes. A detailed study on length dependence of spin filtering is currently underway and is beyond the scope of the current work.

5. CONCLUSION

In conclusion, we have reported successful and reproducible fabrication of individual long CNTs wrapped with single-stranded DNA. Previous studies mostly reported only submicron tubes, but our choice of fabrication parameters allows us to significantly expand (~2–4×) the length range of the tubes. The wrapped tubes have been characterized extensively using various techniques, and they reveal high degree of dispersion of nanotubes, complete DNA wrapping along nanotube length without any evidence of discontinuity and tight physical contact between DNA and nanotube. Such features are highly desirable for subsequent device fabrication.
In particular, long DNA-wrapped tubes are becoming increasingly important in the emerging area of chiral spintronics, where it has been found that longer tubes can increase the spin polarization of charge carriers in electrical transport devices. Initial data suggest the presence of spin filtering in these systems. Our fabrication process enables further investigation in this area (especially, length dependence of spin filtering) and can potentially result in highly spin-polarized nanoscale systems, which will find applications in ultrasmall spintronic devices and circuits.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02237.

Supporting Information is available and contains details of spectroscopic measurements, additional APM, and transport data (PDF)

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Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is funded by NSERC Discovery grant (S.P.) and has been conducted in the Department of Electrical and Computer Engineering, University of Alberta, with the experimental facilities hosted in on-campus nanoFAB and NINT (National Institute for Nanotechnology).

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