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The Unlikely Surfactant: DNA as a Ligand for Single-Walled Carbon Nanotubes

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) were first described almost 20 years ago (Iijima, 1991). Their remarkable properties like mechanical strength, low density, stiffness, chemical and thermal stability, as well as their extraordinary electric and heat conductivity have made them candidates for applications in several areas of nanotechnology. Some of these applications call for pristine carbon nanotubes of a specific chirality. This is particularly true for applications in nanoelectronics. Most production processes generate complex mixtures of metallic and semiconducting SWCNTs, however, making purification a critical step in the overall process. For purification to be successful, several obstacles have to be overcome. One such obstacle is breaking up the very strong interactions between individual carbon nanotubes that lead to bundling. Due to their geometrical structure with a huge length-to-diameter ratio, nanotubes are almost one-dimensional molecules. These cylindrical molecules, which may be regarded as rolled-up graphene sheets, have very hydrophobic properties and engage in extensive van-der-Waals interactions through their π electron-rich surfaces, most probably strengthened by solvophobic effects in polar solvents, such as water. Intermolecular forces sum up over very long distances due to the shape complementarity of the binding partners. Solutions or suspensions of single-walled carbon nanotubes in conventional solvents are therefore metastable, even when the solvents are lipophilic (Liu et al., 1998; Chen et al., 1998; Liu et al., 1999; Bahr et al., 2001; Furtado et al., 2004). To generate suspensions at all, strong mechanical forces, usually in the form of ultrasonication, have to be employed. But, upon time, re-bundling of nanotubes sets in after sonication, again decreasing the interface between tubes and solvent molecules. To overcome the poor solubility, the surface of nanotubes may be modified chemically, resulting in covalently attached functionalities or side chains. Being all-sp² carbon frameworks, whose covalent modification introduces sp³ centers, this necessarily disrupts the electronic structure of the nanotubes (Jung et al., 2004; Cosnier & Holzinger, 2008). Thus, their most characteristic property is often affected in a hard-to-predict fashion with undesirable consequences for any resulting nanostructured device. To obtain pristine, monodisperse nanotubes in solution, bundles have to be broken up and rebundling has to...
be prevented. Experimental work of the last decade has shown that ligands that shield the surface of individual nanotubes immediately after break-up of bundles can indeed lead to suspensions of surprising stability in aqueous solution. Usually, these ligands are amphiphilic molecules with a hydrophobic part and a polar or charged "head group". Amphiphilic molecules with such properties are commonly surfactants. In water, the hydrophobic moiety can associate with the hydrophobic nanotube surface, while the polar part forms an outer shell, well solvated by the surrounding medium. Particularly if a charged head group is involved, the nanotubes thus encapsulated, repulse each other, preventing re-bundling.

2. Solubilization of SWCNTs

2.1 Detergents as Surfactants
Initially, detergents like pyrene salts (Nakashima et al., 2002) and tensides, such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), or sodium cholate (SC) were used to generate stable nanotube suspensions (Ausman et al., 2000; Chen et al., 2001; O’Connell et al., 2002; Islam et al., 2003). The molecular structure of some of these is shown in Figure 1.

![Fig. 1. Structure of most common detergents for solubilization of SWCNTs.](image)

A drawback of these small molecule surfactants is that a large excess of detergent molecules is needed to keep SWCNTs in solution (compare Figure 2), most probably because of the fast off-rate for the complexes with the nanotubes. Removal of the excess surfactant leads to re-bundling of the nanotubes. The free surfactants affect many protocols, though, complicating practical applications and the characterization of the nanotube suspensions.
2.2 Oligonucleotides as Solubilizing Ligands

Overcoming the problem of fast off-rates necessitate the use of a solubilizing ligand that engages in cooperative binding interactions with SWCNTs. Macromolecules may engage in multivalent interactions, resulting in large binding energies for their complexes. These macromolecules may be either synthetic polymers or biomacromolecules. Nanotube suspensions have been obtained with macromolecules like gum arabic (Bandyopadhyaya et al., 2002), amylo maize (Star et al., 2002; Kim et al., 2003), cyclodextrines (Chen et al., 2001; Doidziuk et al., 2003), peptides (Dieckmann et al., 2003; Wang et al., 2003), polymers (O’Connell et al., 2001), or fluorene-based polymers (Chen et al., 2007 a; Nish et al., 2007) as "surfactants". Among the biomacromolecules used to solubilize carbon nanotubes, DNA sticks out as the one producing particularly high yields of solubilized tubes (Figure 2). So, even though its natural role as carrier of genetic information does not suggest that DNA may act as a surfactant, synthetic DNA strands have proven particularly effective in solubilizing single-walled carbon nanotubes and aiding their purification.

Oligodeoxynucleotides - short strands of DNA - may also be attached covalently to SWCNTs (Baker et al., 2002; Dwyer et al., 2002; Hazani et al., 2003; Hazani et al., 2004), but it is the non-covalent complexes (Zheng et al., 2003 a; Nakashima et al., 2003) with nanotubes that we and others find particularly fascinating. They have many favorable properties while retaining the uninterrupted structure of the tubes. For example, very high thermal stability was observed for aqueous suspensions of SWCNTs produced with DNA strands, with half life times of flocculation in the range of many hours at 90 °C (Vogel et al., 2007 a; Vogel et al., 2007 b). Further, suspensions can be obtained with DNA that remain stable for at least one year upon storage at room temperature. Simulations have suggested that close
molecular contacts between DNA and SWCNTs mainly involve the aromatic nucleobases of the oligonucleotides and the surface of the nanotubes (Gowtham et al., 2008). For long single-stranded DNA a helical wrapping around the nanotubes is predicted (Enyashin et al., 2007). This leaves the negatively charged backbone of the oligonucleotides exposed to the solvent (water). The repulsion between the negative charges of the phosphodiesters then efficiently prevents re-bundling. In contrast to small molecule surfactants as solubilizers, excess DNA can be removed from the suspensions of SWCNTs, e.g. by filtration (Kam et al., 2005; Vogel et al., 2007a), without flocculation of the tubes. Due to their shape, nanotubes cannot pass through the channels inside membrane of the filter, whereas the more globular, unbound DNA molecules are enriched in the filtrate of the centrifugation. After filtration, DNA-SWCNT complexes retained on the filter can be resuspended.

Synthetic DNA has the advantage of being available in monodisperse form with any given sequence of the four canonical nucleobases (A/C/G/T) at moderate cost. So, once DNA was established as a good solubilizing agent for SWCNTs, several groups set out to find the optimal DNA sequence and strand length to solubilize a maximum amount of nanotubes. The first group to systematically vary sequence and length of the oligonucleotide solubilizer was that of Tassi, Walls and colleagues at DuPont (Zheng et al., 2003a; Zheng et al., 2003b). Their work suggested that sequences of poly d(T) and alternating sequences of deoxyguanosine and thymidine of a length of 20 to 90 nucleotides (d(GT)) were best suited for generating concentrated suspensions suitable for purification. Another group questioned these conclusions (Gigliotti et al., 2006). They solubilized nanotubes with single-stranded DNA of 100 nucleotides average length and found that shorter stands, consisting of approx. 50 nucleotides, and made up of mixed sequences, yielded lower amounts of solubilized SWCNTs. It was then reported that SWCNTs can be solubilized by very long single-stranded DNA (> 1000 nucleotides) produced by amplification (Zhao et al., 2006) and asymmetric polymerase chain reaction, PCR (Liang et al., 2007). Others had found independently that double-stranded DNA can be used to obtain very concentrated suspensions (Barisci et al., 2004), but it is not clear whether denaturation of the duplexes occurred during the solubilization protocol, making single-stranded DNA the relevant species in solution. Studies with single nucleotides, like 2'-deoxyadenosine-5'-diphosphate and 2'-deoxyguanosine-5'-monophosphate, as surfactants also produced fairly concentrated nanotube suspension (Ikeda et al., 2006), but it was not studied in detail what the kinetic stability of these suspensions is. As expected, mononucleotides with the smaller and less lipophilic pyrimidine nucleobases uracil and cytosine proved to be poorer surfactants for solubilization of SWCNTs than their purine counterparts.

The solubilization of SWCNTs with modified, thiol-terminated oligonucleotides was reported in 2007 (Han et al., 2007). The group described an assembly of gold nanoparticles and the DNA-SWCNT complexes, in which the sulfur of the former thiol groups of the oligonucleotides binds to the nanoparticle surface. Atomic force microscopy (AFM) showed nanoparticles in the immediate vicinity of nanotubes. This is an early example of hybrid complexes in which the (modified) DNA acts as the "molecular glue", holding together complexes with SWCNTs.

Because of the diverse set of results obtained by different researchers, our own group performed a detailed study on the length and sequence dependence of the solubilizing power of synthetic DNA used as surfactants for HiPco SWCNTs (Vogel et al., 2007a; Vogel et al., 2007b). Oligonucleotides with sequences of d(AC)_n and d(GT)_n with n = 2, 3, 5, 10, 20,
and 40, as well as mixtures of equal length strands of both sequences were employed. A maximum amount of HiPco tubes was solubilized with a mixture of the two hexamers \( d(AC)_n \) and \( d(GT)_n \). Surprisingly, longer oligonucleotides yielded less concentrated suspensions. Loh and coworkers also reported that longer oligonucleotides interact less well with nanotubes and show looser wrapping around the tubes, as confirmed by AFM, Raman and photoluminescence measurements (Yang et al., 2009). Work by Kim and colleagues demonstrated enrichment of (6,5)-nanotubes when using genomic, salmon DNA (Kim et al., 2008), which may or may not be the result of sequence-specific interactions, as genomic DNA contains a range of different sequence motifs. As detailed below, our own work on DNA-SWCNT complexes now employs sequences with a high propensity to fold, leading to stable intramolecular structures (Müller et al., 2009).

Studies of the kind mentioned above benefit from the fact that the nanotube content of suspensions can be determined directly from UV-Vis/NIR absorption spectra, using inexpensive instrumentation. The absorption spectra also provide a good first impression of the composition of the nanotube mixture. Figure 3 shows such spectra of samples prepared in our lab from HiPco SWCNTs (black line) or CoMoCAT tubes (red line). The advantage of CoMoCAT tubes as starting material is its richness in certain chiralities, particularly (6,5)-tubes that are formed selectively during the production process (Tan & Resasco, 2005). A characteristic absorption peak of CoMoCAT nanotubes appears at a wavelength of 989 nm (see Figure 3) and its intensity may be taken as a measure of solubilized nanotubes. Since bundles often produce a broad background signal, the absorption value should be corrected for the background, measured e.g. at 1090 nm. More detailed information on the composition of nanotube samples may be obtained from photoluminescence (PL) maps (O’Connell et al., 2002).

![Absorption spectra of HiPco and CoMoCAT SWCNTs solubilized with DNA as surfactant. Both prominent peaks in the CoMoCAT spectrum can be assigned to the E_{11} (989 nm) and E_{22} (575 nm) transitions of (6,5)-nanotubes, respectively. The HiPco sample (black line) contains many different chiralities, and the spectrum is a superposition of absorption spectra of different (n,m)-nanotubes.](image-url)
3. Purification and Separation of SWCNTs

3.1 General Methods
While solubilizing nanotubes in aqueous media may be a mature technology, separating the mixtures of different tube diameters, chiralities and lengths into samples of uniform structures certainly is not. For more demanding applications, e.g. in nanoelectronics, such a separation is highly desirable, if not necessary. There are some techniques producing nanotubes within a small diameter range that, together with improved separation techniques, may yield spectrally uniform SWCNTs of a high purity. Enrichment of either semiconducting or metallic SWCNTs by chemical conversion of nanotubes has also been reported. Other approaches, relying on non-covalent complexes, allow for enrichment of nanotube species without covalent alteration of their structure. Dielectrophoresis (Krupke et al., 2003; Lee et al., 2005) and density gradient ultracentrifugation (Arnold et al., 2005; Arnold et al., 2006) have been used in several studies to enrich metallic nanotubes or nanotubes with a specific diameter/chirality. Separation by density gradient ultracentrifugation has led to semiconducting tubes enriched in (6,5)- and (7,5)-tubes (Arnold et al., 2006; Crochet et al., 2007). A different approach is based on extraction after polymer wrapping SWCNTs (Shigeta et al., 2006). Finally, fluorene-based polymers have a high preference to extract individual species of SWCNTs (Chen et al., 2007 a; Nish et al., 2007). Selectivity for specific (n,m)-species apparently relies on the stability of specific SWCNT-polymer complexes in solution. "Chirality" is used loosely, though, as nanotube suspensions are usually optically inactive, containing equal amounts of left- and right-handed tubes. But, using diporphyrins (chiral "nano-tweezers"), Osuka and coworkers enriched nanotubes of a defined handedness to obtain optically active SWCNT samples (Peng et al., 2007).

3.2 DNA-assisted Separation and Purification
Interestingly, DNA has been reported not only to produce stable nanotube suspensions, but also to facilitate nanotube separation (Zheng et al., 2003 a; Strano et al., 2004). It was reported that complexes of certain DNA sequences and SWCNTs, when submitted to ion-exchange chromatography, separate into individual fractions enriched in semiconducting or metallic tubes (Zheng et al., 2003 a; Zheng et al., 2003 b). In addition, size-exclusion chromatography of DNA-solubilized nanotubes has led to samples of nanotubes with a narrow length distribution (Huang et al., 2005; Bauer et al., 2007; Bauer et al., 2008). The researchers described a separation of DNA-coated SWCNTs by size, using flow-field fractionation (Chun et al., 2008). Dai and coworkers reported separation of HiPco-grown nanotubes solubilized with DNA by length, diameter, and chirality with different chromatography methods (Zhang et al., 2008). They combined size-exclusion chromatography and ion exchange chromatography and identified the chiral vector of the nanotubes by photoluminescence excitation spectroscopy, absorption spectroscopy, and electrical transport measurements. One of the most recent publications described certain DNA sequences, identified from a DNA "library", that wrap preferentially around semiconducting SWCNTs of one specific chirality (Tu et al., 2009). The authors write that they have separated more than 10 types of nanotubes of different chiralities from HiPco material by ion-exchange chromatography. The fractions were characterized mainly by optical absorption spectroscopy. The authors also presented structures of hydrogen bonded...
antiparallel non self-complementary dodecamer strands on a nanotube that they obtained by modeling. They hypothesize that each of these DNA barrel structures is formed on a particular (n,m)-nanotube. It will be interesting to see whether direct experimental evidence for the base pairs proposed can be obtained.

![Fig. 4. The shape of double stranded DNA and (6,5)-nanotubes, as seen perpendicular to the helix axes (left-hand side) or along the helix axes ("top view", right-hand side). Structures are drawn to scale to visualize shape complementarities (or lack thereof).](image)

Coordinates of the nanotube were generated with TubeGen 3.3 (http://turin.nss.udel.edu/research/tubegenonline.html by Frey and Doren, University of Delaware, Newark DE, 2005) and visualized using VMD (Humphrey et al., 1996).

Fundamentally, there is no simple shape complementarity between base-paired, canonical duplex DNA and carbon nanotubes. This can be seen from an inspection of Figure 4. The DNA double helix does not have a central hole that could accommodate even a small (6,5)-nanotube, and neither of the two grooves is sufficiently large or hydrophobic to bind to tubes.

4. Assemblies

4.1 Overview

Oligonucleotides are attractive nanoscale building blocks because they are addressable sequence-specifically. It is therefore an interesting question to what extent complexation of oligonucleotides with SWCNTs blocks the ability of the DNA to form duplexes with complementary strands. If the adsorption on the tube surface forces the DNA to adopt a conformation that is incompatible with Watson-Crick duplexes, the programmable recognition capability of the DNA will be lost. Further, if multivalent interactions or unspecific interactions dominate, the strength of the interactions will be difficult to program into the DNA sequences and difficult to control on the experimental level. Currently there is no general answer to these questions, but some encouraging results have been obtained. For example, hybridization between strands of partly DNA-wrapped SWCNTs has been reported to induce the formation of aggregates (Figure 5a). Furthermore, hybrid structures
of SWCNTs and gold nanoparticles (AuNP) have been generated, based on hybridization (see Figure 5b) (Chen et al., 2007 b). The new materials were analyzed by gel electrophoresis, dynamic light scattering (DLS), optical absorption spectroscopy, and atomic force microscopy (AFM). In the case of nanotube assemblies (Figure 5a), the authors measured a decrease in absorbance. For the hybrid materials (Figure 5b), AFM images showed evidence for SWCNT-AuNP complexes. In either case, the DNA-SWCNT complexes were generated by sonicating the tubes with SDS as surfactant and a probe sonicator, followed by ultracentrifugation. Afterwards single-stranded DNA was added at room temperature without any further sonication. Under these conditions, the DNA strands may not displace more than a small fraction of the SDS on the tubes. Being only loosely bound to the surfactant-wrapped tubes, much of the base pairing capability of the DNA may be retained.

In a related study, controlled aggregation of nanotubes mediated by hybridizing DNA strands (Li et al., 2007) was induced by two different strategies (Figure 6). The first, dubbed "tail strategy" involves a hybridizable tail of the nanotube-wrapping oligonucleotide that forms a duplex with a so-called splint strand. The second strategy, referred to as "tail-free strategy" involves direct hybridization of two tube-wrapping single strands. The former strategy gave much faster hybridization kinetics than the latter strategy. The authors state that in the latter case the DNA sequences have a strong tendency to wrap around the SWCNTs, leading to a dramatically decrease in base pairing ability. For this study, DNA-SWCNT complexes were obtained by sonication for 30 min with a probe sonicator under ice cooling, followed by ultracentrifugation for 1 h. In the "tail strategy" the mediating splint strands were added after the solubilization step to pre-formed DNA-SWCNT suspensions. Again characterization relied on gel electrophoreses and AFM.

So, there are ways to make tube-bound DNA strands addressable to complementary sequences. In our experience, it is difficult to prevent overhang DNA from adsorbing to the remaining free tube surfaces, though, making designs that require unbound portions of partially bound strands dependant on exquisite control over kinetic parameters. Further, once DNA-induced complex formation has occurred, the size of the aggregates can make characterization difficult.
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of SWCNTs and gold nanoparticles (AuNP) have been generated, based on hybridization (see Figure 5b) (Chen et al., 2007b). The new materials were analyzed by gel electrophoresis, dynamic light scattering (DLS), optical absorption spectroscopy, and atomic force microscopy (AFM). In the case of nanotube assemblies (Figure 5a), the authors measured a decrease in absorbance. For the hybrid materials (Figure 5b), AFM images showed evidence for SWCNT-AuNP complexes. In either case, the DNA-SWCNT complexes were generated by sonicating the tubes with SDS as surfactant and a probe sonicator, followed by ultracentrifugation. Afterwards single-stranded DNA was added at room temperature without any further sonication. Under these conditions, the DNA strands may not displace more than a small fraction of the SDS on the tubes. Being only loosely bound to the surfactant-wrapped tubes, much of the base pairing capability of the DNA may be retained.

Fig. 5. DNA hybridization controls aggregation of SWNTs (a) and formation of SWNT-gold nanoparticle hybrid structures (b). Reprinted with permission from Chen et al., 2007b. Copyright 2007 American Chemical Society.

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Fig. 6. Self-assembly of DNA-coated carbon nanotubes into 3D aggregates through hybridization: Tail strategy (a) and tail-free strategy (b). Reproduced with permission from Li et al. 2007, Copyright Wiley-VCH Publishers.

In yet another study by Tan and coworkers, DNA adsorbed on nanotubes was shown to engage in base pairing with other DNA strands. In one of their publications, this group chose a molecular beacon (MB) DNA motif (Yang et al., 2008a). An MB is a single-stranded oligonucleotide with self-complementary ends linked by a sequence of non-complementary nucleotides in the middle. If the ends form an intramolecular duplex, the resulting structure has the shape of a hairpin. If both ends of the hairpin are labeled, one with a fluorophore and the other with a quencher, breaking up the hairpin separates fluorophore and quencher, with concomitant increase in fluorescence intensity. The term "molecular beacon" is used in analogy to the beacons that lead mariners approaching the land. Molecular beacons are interesting tools for studying the often enigmatic interactions between DNA and SWCNTs. In the study mentioned above, complexes of SWCNTs and MBs were treated with an oligonucleotide complementary to the MB, leading to a structural change from hairpin to an extended, intermolecular duplex (Figure 7). Hybridization led to the expected change in fluorescence intensity. Apparently, hybridized beacons are unable to hold on to nanotubes.

Fig. 7. Structural transitions in complexes of molecular beacons and SWNTs. Reprinted with permission from Yang et al., 2008b. Copyright 2008 American Chemical Society.
In another study, the same authors described a new class of fluorescing sensors for biomolecular interactions, based on assemblies of SWCNTs and single-stranded DNA (Yang et al., 2008 b). Again, changes in fluorescence intensity were measured. When the fluorophore is in the vicinity to the nanotube, its fluorescence is quenched by the tube. Upon hybridization with a complementary strand, the fluorescence is recovered because the fluorophore-bearing duplex is released from the nanotube surface. The SWCNT-DNA complexes were prepared as follows. First, nanotubes were solubilized in dimethylformamide (DMF) by sonication with a probe sonicator for 5 h, followed by the addition of oligonucleotides and incubation for 5-15 min. Finally the hybridization partner was added, and after a few hours, the mixture was submitted to ultracentrifugation. So, all hybridization experiments with non-covalent DNA-nanotubes complexes have one important detail in common: Successful hybridization is favored by a protocol in which the DNA is not present during sonication with the probe sonicator. Instead, adsorption of the DNA to be addressed on the SWCNTs is usually induced after nanotube suspensions have been generated. This may explain why we found DNA adsorbed during the sonication step to be unaddressable (Vogel et al., 2007 a), whereas groups did not.

4.2 Outlook: Towards DNA-Mediated Nanostructuring

How may the programmable molecular recognition properties of DNA be harnessed to steer DNA-coated SWCNTs into designed three-dimensional architectures, based on predictable base pairing interactions? While results from recent studies are promising, significant challenges remain. Many of the complexes used are metastable. Keeping the SWCNT-DNA complexes within their local minimum in the energy landscape is difficult. Small changes in the chemical environment can trigger decomposition of these complexes. If sufficient kinetic energy is applied, as during sonication with a probe sonicator, DNA will fully denature and then adsorb in a conformation that makes it unavailable for base pairing. In these unproductive complexes, oligonucleotides are probably fully extended and fully wrapped around the nanotubes, leaving no unbound overhang that can be addressed with a complementary sequence. Transmission electron microscopy images seem to confirm this view (Malik et al., 2007). Even if a metastable state is established, with sufficiently high activation barriers preventing re-bundling of the tubes or conformational changes in the DNA, binding to specific positions in very long nanotubes is not yet feasible. Even if it was, the sheer strength of the multivalent interactions between nanotubes and surfaces or other nanoscale objects will continue to make it difficult to place an individual SWCNT at a precise location in a designed, DNA-driven structure. Single-walled carbon nanotubes are not only molecules with unusual electronic properties; they are also very large molecules with a massive intrinsic binding energy!

Ideally, one would want to develop a receptor-like DNA folding motif that binds to a specific nanotube chirality and retains its ability to engage in base pairing. Extensive searches in DNA sequence space have led to some oligonucleotides with surprising selectivity (Tu et al., 2009). Still, these oligonucleotides have not been shown to be available for conventional intermolecular base pairing. We believe that a combination of DNA strands and suitable surfactants may lead to complexes that do both bind and remain addressable. If free nanotube surface areas between DNA binding sites are covered with surfactant, adsorption of addressable overhangs of DNA strands may be kept from adsorbing. Further, assembling tight and specific coatings from a suitable combination of small molecules and nanoscale objects will continue to make it difficult to place an individual SWCNT at a precise location in a designed, DNA-driven structure. Single-walled carbon nanotubes are not only molecules with unusual electronic properties; they are also very large molecules with a massive intrinsic binding energy!
oligonucleotides should be simpler and less expensive than wrapping long nanotubes in a single polynucleotide of a length inaccessible by conventional DNA synthesis. Addressability of the DNA may then be achieved by employing higher order structures, such as triplexes, quadruplexes, or I-motifs (Nonin et al., 1997; Zhao et al., 2009).

So, to get addressable nanotubes, we assume that it is useful to identify a combination of surfactants and structured DNA. We are currently engaging in a project with this goal, using a two-step protocol. First, the SWCNTs are dispersed with surfactants only, without DNA. Then, folded (pre-structured) DNA is added under conditions under which no more than partial wrapping of the tubes is expected. To obtain nanotubes suitable for generating nanostructured electronic devices, we employ tubes of the greatest sample homogeneity possible. Currently, we apply a literature-known density gradient ultracentrifugation protocol to further enrich CoMoCAT SWCNTs in (6,5)-tubes. This protocol employs a gradient of iodixanol and a buffer containing two weight percent of a mixture of sodium cholate and sodium dodecyl sulfate (Arnold et al., 2006; Crochet et al., 2007). Since nanotubes of different diameters have different densities, ultracentrifugation yields bands containing nanotubes of the same diameter. We then expose the pre-purified and cholate-wrapped tubes to oligonucleotides folded to a loop designed to bind the nanotubes. To demonstrate that the DNA bound to the SWCNTs is indeed an addressable binding motif, we use hybridization assays with fluorophore-labeled complementary strands. Control experiments with labeled strands of a different sequence are critically important to demonstrate that binding is not the result of unspecific interactions that do not rely on base pairing. Binding equilibria can be studied by using filters that retain the nanotubes, but allow unbound DNA to pass. In either sample (with complementary and non-complementary DNA) the tubes retained on the filter are resuspended and the resulting solutions studied by fluorescence spectroscopy. Similar experiments can be performed with quantum dots (QDs) as nanoscale "cargo", bound to DNA-coated SWCNTs (Müller et al., 2009). Centrifugation separates bound from unbound species, allowing one to determine binding constants and to establish sequence-specific base pairing.

5. Conclusion

In this chapter, oligonucleotide-SWCNTs complexes are discussed, emphasizing that DNA has surfactant properties that make it useful for solubilizing carbon nanotubes. Stable, largely monodisperse suspensions can be obtained after sonication and separation processes, such as density gradient ultracentrifugation. In ideal cases, complexes are obtained that are predominantly of a single nanotube diameter and chiral index and that engage in sequence-specific base pairing interactions. Based on models of unperturbed duplex DNA, it appears as if there was no shape complementarity between DNA duplexes and single-walled carbon nanotubes. So, when the DNA adsorbs on the nanotube surface, it can be expected to be distorted so much that it loses its ability to form Watson-Crick duplexes where T pairs with A and G pairs with C. DNA-mediated nanostructuring involving SWCNT-DNA complexes may be achieved by generating complexes where part of the DNA strands remains unbound. Usually, such complexes are metastable structures, since full adsorption of the DNA would lead to a thermodynamically more stable structure. Unpublished results from our laboratories shows that such kinetically stable, addressable DNA can be generated from stably folded DNA motifs. Engaging them in sequence-specific

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base pairing interactions constitutes an important step towards nanoconstruction with carbon nanotubes. Since DNA is one of the most powerful materials for soft matter nanostructuring (Park et al., 2008; Nykypanchuk et al., 2008; Meng et al., 2009), and consequently, DNA nanostructuring is one of the fastest growing fields of present-day science, (Niemeyer, 1999; Seeman, 2003; Gothelf and LaBean, 2005; Lu et al., 2008; Shin et al., 2009), we believe that harnessing the complexes the DNA and SWCNTs will lead to the discovery of fascinating new functional nanomaterials.

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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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