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DNA-Wrapped Carbon Nanotubes: From Synthesis to Applications

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1. Introduction

Carbon nanotubes (CNTs) have been the focal point of many studies since their discovery two decades ago (Iijima, 1991). They are allotropes of carbon with cylindrical shape and sp² hybridization, which are formed by benzene-type hexagonal rings of carbon atoms. CNTs can be classified as either single-walled (SWNTs) or multi-walled carbon nanotubes (MWNTs) depending on their structure. They possess a very high aspect ratio (i.e. length/diameter), with diameters in the range of nanometers and lengths that can reach microns. Additionally, CNTs can be divided according to their conductivity, into metallic or semiconducting tubes.

Nanotubes possess outstanding structural, mechanical and electronic properties due to the unique combination of their dimension, structure and topology. For example, CNTs are extremely strong, can be highly conducting, and exhibit high thermal and chemical stability (Mintmire et al., 1993; Mintmire & White, 1998). Also, they are elastic and have many times the tensile strength of steel (Service, 1998). Due to these unique properties, CNTs have been proposed for many applications, ranging from scanning probes (Dai et al., 1996) and hydrogen storage (Dillon et al., 1997), to biosensors (Nguyen et al., 2002).

Several methods have been commonly used to synthesize CNTs, including arc discharge, chemical vapor deposition and laser ablation, among others (Ando et al., 2004). After the growth process, CNTs contain impurities such as metal catalyst nanoparticles, amorphous carbon, carbon nanoparticles, and fullerenes, which must be removed. Typical CNTs purification techniques include ultrasonication (Shelimov, et al., 1998), microfiltration (Bandow et al., 1997), chromatographic techniques (Nigoyi et al., 2001), microwave heating (Harutyunyan et al., 2002), gas-phase oxidation (Ebbesen et al., 1994), and acid oxidation (Rinzler et al., 1998). Nevertheless, their purification is not a trivial task, and either improvement on the existing techniques or development of new purification methodologies are required in order to facilitate the use of CNTs and their integration into nanodevices and composite materials.

Another main challenge to overcome is the need for the development of new functionalization chemistries that can increase the solubility of CNTs without altering their
properties. Carbon nanotubes are extremely difficult to manage due to their low solubility in both aqueous and organic solvents, which restricts the extent of their applications. To increase the solubility of CNTs opens many possibilities, such as simplifying the purification process and making the nanotubes more manageable, which consequently facilitates their use as standard chemical reagents.

One of the first and more commonly used approaches to increase the solubility of carbon nanotubes is to use strong acids to attack and shorten the tubes (Liu et al., 1998). Even though this method is effective in increasing the CNTs solubility, it has the disadvantage of getting rid of one of the attractive properties of the nanotubes: their high aspect ratio. Since then, different approaches using chemical functionalization have been probed in order to increase the solubility and manageability of CNTs without altering their desirable properties.

2. Non-covalent functionalization of carbon nanotubes

Chemical functionalization has been the most successful method to solubilize CNTs thus far. Functionalization of CNTs offers many advantages such as: improving the solubility of the nanotubes, transforming them into more manageable materials, and combining the unique properties of CNTs with those of other materials.

Chemical functionalization of CNTs can be achieved by either non-covalent or covalent interactions. Contrary to covalent functionalization methods, which disrupt the extended π-networks on the CNTs surfaces and can modify their mechanical and electronic properties, non-covalent functionalization preserves the desired properties of CNTs, at the same time as it improves their solubility. The non-covalent functionalization of CNTs has been performed with molecules as diverse as polymers, biomolecules, surfactants, and polyaromatic compounds (Tasis et al., 2006). The main driving forces for the non-covalent interaction between the CNTs and these molecules are van der Waals and π-stacking forces.

A wide range of polymers have been used in the formation of supramolecular complexes of CNTs including, among others, polyvinyl pyrrolidone, polystyrene sulfonate, poly(1-vinyl pyrrolidone-co-vinyl acetate), dextran, dextran sulfate, poly(1-vinyl pyrrolidone-co-acrylic acid), poly(1-vinyl pyrrolidone-co-dimethylaminoethyl methacrylate), bovine serum albumin, starch and deoxyribonucleic acid (DNA) (O’Connell et al., 2001; Star et al., 2002; Zheng et al., 2003a).

The formation of supramolecular complexes between DNA and CNTs has drawn much attention in the past years, since these hybrids can take advantage of the unique properties of the nanotubes and the remarkable recognition capabilities of DNA. DNA-wrapped CNTs exist as a well-defined chemical entity in aqueous solution due to the strong non-covalent interaction between the DNA and the CNTs (Zheng, 2007). Compared to other polymers used, DNA offers the advantage of defined length and sequence, high dispersion efficiency (i.e. up to 4 mg/mL) and well-developed chemistries for further functionalization of the DNA-CNT hybrid through either covalent or non-covalent functionalization (Zheng et al., 2003a).

In the next sections of this chapter, we will describe the different methods used to synthesize DNA-wrapped CNTs, as well as the main techniques employed to characterize these complexes in both aqueous solutions and solid substrates. In addition, the main applications of the DNA-CNT complexes will be discussed.
3. DNA-wrapped carbon nanotubes

3.1 Synthesis
The first reports on the synthesis of DNA-wrapped CNTs were published by several groups in 2003 (Zheng et al., 2003a; Dovbeshko et al., 2003a; Dovbeshko et al., 2003b; Nakashima et al., 2003; Zheng et al., 2003b). The preparation of the DNA-wrapped CNTs complexes is a simple and straightforward procedure, which consists on adding the CNTs to an aqueous solution of DNA, and then mixing the components by stirring and/or sonicating in an ice-water bath. Wrapping of the CNTs by DNA (Fig. 1) occurs when the aromatic hydrophobic DNA bases interact with the sidewall of the CNT via π-stacking, whereas the hydrophilic sugar-phosphate backbone of the DNA strand is left exposed to interact with the aqueous solvent (Zheng et al., 2003a). Changes in either the type of DNA or CNTs used are common variations to the synthesis methodology. For example, Dovbeshko and coworkers synthesized the DNA-CNT complexes by using denatured calf thymus DNA and SWNTs produced by the arc discharge method (Dovbeshko et al., 2003a; Dovbeshko et al., 2003b). Nakashima’s group, in contrast, used purified HiPCO (High-Pressure CO conversion) SWNTs and a solution of DNA from salmon testes (Nakashima et al., 2003). On the other hand, Zheng et al. reported the first time use of short synthetic oligonucleotide sequences for the preparation of DNA-wrapped CNTs (Zheng et al., 2003a; Zheng et al., 2003b). In addition to short synthetic DNA strands (Zheng et al., 2003a) and denatured genomic DNA (Dovbeshko et al., 2003a; Dovbeshko et al., 2003b; Gigliotti et al., 2006), CNTs have been dispersed and functionalized with short fragmented DNA (Gladchenko et al., 2006; Xu et al., 2007), DNA synthesized by asymmetric polymerase chain reaction (PCR) (Liang et al., 2007), and single-stranded DNA (ssDNA) obtained by rolling circle amplification (Zhao et al., 2006). Some reports have also shown that long denatured fragments of lambda DNA (Gigliotti et al., 2006) and double-stranded DNA (dsDNA) produced by symmetric PCR (Liang et al., 2007) lacked the capability to efficiently wrap around and disperse the CNTs.

Fig. 1. Graphical representation of an ss-DNA-wrapped single-walled carbon nanotube. Reprinted with permission from (Ma et al., 2006a). Copyright (2006) American Chemical Society.

Many studies have been performed in order to optimize the dispersion efficiency of CNTs in DNA. Variations in parameters such as DNA sequence, DNA length, sonication time, type
of CNTs, and solvent conditions, have been reported. For example, the first report on the effect of DNA sequence and length on the dispersion efficiency showed that among 60-mer homopolymers, poly(T) resulted in the best yield, whereas among the four different lengths of poly(T) studied (15, 21, 30 and 60), T30 displayed the highest dispersion efficiency (Zheng et al., 2003a). Additionally, d(GT)ₙ (with n = 10 to 45) DNA sequences have been shown to have both a high dispersion yield and the highest efficiency in facilitating CNTs separation by diameter and type with anion exchange chromatography (Zheng et al., 2003b). A subsequent report demonstrated that shorter DNA sequences unexpectedly displayed excellent dispersion yields, and that a mixture of the complementary oligonucleotides d(GT)ₙ:d(AC)ₙ showed the highest efficiency among all the sequences studied (Vogel et al., 2007). Additionally, a recent study showed that the compactness and selectivity of DNA wrapping around SWNTs are dependent on the length of the DNA sequence, and that by increasing the strand length, both the degree of compactness of the wrapping around the nanotube and the diameter selectivity decrease (Yang et al., 2009).

A study on the effects of sonication time and CNT type on the dispersion efficiency of CNTs by DNA showed that sonication times higher than 90 minutes were required with poly(T)₃₀ in order to obtain well-dispersed individual DNA-wrapped CNTs (Lahiji et al., 2007). Increasing the sonication time to 120 minutes increased the dispersion efficiency, but decreased the size of the CNTs, suggesting that they break during long sonication periods. Moreover, CNTs synthesized by electric-arc (EA) and HiPCO processes were compared and the results demonstrated the presence of particulates or impurities in the EA sample that were not observed in the HiPCO CNTs. These observations confirmed that the purity of as-received HiPCO CNTs is higher than that of EA CNTs. As-received and chemically oxidized CNTs were also compared after DNA wrapping. The oxidized CNTs had a shorter length and showed an increase in the number of DNA molecules on the CNT surface. Variations in solvents and DNA:CNT ratios have also been studied. For instance, it has been reported that the dispersion efficiency can be increased by changing the solvent from normal water (H₂O) to deuterated water (D₂O) (Yang et al., 2007b). Additionally, the results of this study showed that CNTs with small diameters are preferentially dissolved in D₂O, whereas larger diameters CNTs are easily dissolved in H₂O. On the other hand, Taeger and collaborators reported that the best dispersion efficiency is achieved at DNA:CNT ratios of 1:1 or 1:2 (Taeger et al., 2005). Furthermore, a ratio of 1:2 is preferred, since it minimizes the amount of unbound DNA.

In contrast to the typical approach for creating DNA-wrapped CNTs, which requires sonication, milling has also been used to synthesize the DNA-CNT complexes. Nepal and coworkers reported the synthesis of DNA-wrapped CNTs based on a solid-state mechanochemical reaction (Nepal et al., 2005). Their “one-pot synthetic method” consisted on adding CNTs and DNA to a ball-milling apparatus, and milling the mixture for 30 minutes to 1 hour. Aqueous solutions of DNA-wrapped CNTs with high stability (> 6 months), and a uniform length distribution were obtained. Additionally, a high-speed vibration milling technique was used to solubilize SWNTs with nucleotides (Ikeda et al., 2006). The dispersion efficiency was dependent on the type of base used and the number of phosphate groups. Finally, DNA-wrapped CNTs have been used as a template to create more complex conjugates. DNA-CNTs have been functionalized with platinum nanoparticles (Ostojic, et al., 2008), quantum dots (Campbell et al., 2007), cytochrome c (Heering et al., 2006), biotin-
avidin-biotin conjugated antimouse IgG (Cao et al., 2009), gold nanoparticles (Li et al., 2007; Chen et al., 2007), a photosensitizer (Zhu et al., 2008), and other DNA-wrapped nanotubes (Li et al., 2007; Chen et al., 2007), and they have also been incorporated into a polymeric film (Ma et al., 2006a; Ma et al., 2006b). Hersam’s group, for example, used cisplatin and potassium tetrachloroplatinate as DNA cross-linkers and subsequently reduced the bound platinum salts to functionalize the DNA-CNT complexes with platinum nanoparticles (Ostojc, et al., 2008). This methodology provided strong binding between the Pt nanoparticles and the DNA without perturbing the desirable properties of the nanotubes. The prepared Pt/DNA-CNT complexes might find use in applications as diverse as fuel cells and biosensors.

Thiol-functionalized DNA strands have also been used to attach gold nanoparticles and quantum dots to DNA-CNT conjugates. Rigid arrays of gold nanoparticles aligned on the surface of CNTs were obtained by Han and coworkers through the bonding between the thiol group in the modified DNA strands wrapped around the CNTs, and the gold nanoparticles (Han et al., 2007). DNA-wrapped CNTs were also functionalized with CdSe/ZnS quantum dots by using thiol-modified DNA wrapped around the nanotubes (Campbell et al., 2008). The binding of the quantum dots to the DNA-CNT complexes allowed the elucidation of the location of the DNA strands on the nanotube surface by atomic force microscopy. Conversely, two groups functionalized DNA-wrapped CNTs with gold nanoparticles and with other DNA-wrapped CNTs (Fig. 2) though hybridization between complementary DNA sequences (Li et al., 2007; Chen et al., 2007).

On the other hand, a composite between poly-(anilineboronic acid) and DNA-wrapped CNTs was prepared by Ma et al. by in situ polymerization of 3-aminophenylboronic acid) in the presence of the DNA-CNT complexes. The resultant composites showed enhanced stability, conductivity and redox chemistry.

Fig. 2. Schematic representation of the complexes formed between several DNA-wrapped CNTs modified with complementary DNA sequences (left), and between a DNA-wrapped CNT and Au nanoparticles modified with complementary DNA strands (right). Reprinted with permission from (Chen et al., 2007). Copyright (2007) American Chemical Society.

3.2 Main properties and characterization
DNA-wrapped CNTs have been studied by numerous techniques, including among others, atomic force microscopy (AFM) (Zheng et al., 2003a; Nakashima et al., 2003; Zheng et al., 2003b; Taeger et al., 2004; Takahashi et al., 2006), transmission electron microscopy (TEM) (Nakashima et al., 2003; Zhao et al., 2006; Rajendra, et al., 2004; Malik et al., 2007; Ikeda et al., 2006; Shoda et al., 2009), Raman spectroscopy (Dovbeshko et al., 2003a; Dovbeshko et al.,
2003b; Zheng et al., 2003b; Shoda et al., 2009; Chou et al., 2004a; Kawamoto et al., 2006a; Kawamoto et al., 2006b; Yang et al., 2007a), Fourier transform infrared spectroscopy (FTIR) (Dovbeshko et al., 2003a; Dovbeshko et al., 2003b), absorption spectroscopy (Zheng et al. 2003a; Nakashima et al., 2003; Zheng et al., 2003b; Malik et al., 2007; Meng et al., 2007; Nair et al., 2006), scanning electron microscopy (SEM) (Sánchez-Pomales et al., 2007a; Nepal et al., 2005; Li et al., 2007; Hu et al., 2005; Karachevtsev et al., 2006a), fluorescence spectroscopy (Nepal et al., 2005; Strano et al., 2004; Hobbie et al., 2005; Luo et al., 2006; Fagan et al., 2007b), scanning tunneling microscopy (STM) (Iijima et al., 2005; Yarotski, et al., 2009), small angle neutron scattering (Hobbie et al., 2005), optical microscopy (Badaire et al., 2005; Li et al., 2009), photoluminescence spectroscopy (Luo et al., 2006; Chou et al., 2005; Torrens et al., 2006), energy dispersive spectroscopy (EDS) (Sánchez-Pomales et al., 2007a; Hu et al., 2005), capillary electrophoresis (Khripin et al., 2009b) and electrochemistry (Hu et al., 2005; Li et al., 2009; Heering et al., 2006; Napier et al., 2005).

Specifically, the structural properties of the DNA-wrapped CNTs have been studied by AFM, Raman spectroscopy and photoluminescence spectroscopy, among others. For example, Qian and coworkers were able to differentiate between DNA-wrapped and unwrapped CNT segments by using high-resolution tip-enhanced near-field microscopy to monitor the photoluminescence energy shift along the nanotube surface (Qian et al., 2008). In another study it was reported that SWNTs induce destabilization and a B-A transition on DNA, and that these processes depend on the DNA sequence (Li et al., 2006).

Atomic force microscopy and photoluminescence spectroscopy results showed that diminishing the nanotube concentration could decrease the mean bundle diameter in DNA-SWNTs dispersions (Cathcart et al., 2008). The results demonstrated that once a dispersion of DNA-SWNTs is obtained, spontaneous debundling occurs upon dilution, which means that dispersions with a higher content of individually dispersed nanotubes can be obtained without the need for additional sonication. Toita and coworkers prepared DNA-SWNTs dispersions with nanotubes synthesized by two methods: HiPco and arc discharge (Toita et al., 2008). Their AFM study suggests that the DNA-wrapping mechanism for SWNTs prepared by arc discharge may be different from HiPco SWNTs due to differences in nanotube diameters. A dependence on the diameter was also reported in a study of DNA-wrapped CoMoCAT SWNTs (Chou et al., 2004).

Additionally, a study on the time dependence of DNA wrapping in SWNTs dispersions was performed with photoluminescence (Cathcart et al., 2008). Photoluminescence intensity increased over time, and this observation was correlated to the formation of a monolayer coating of DNA on the nanotube walls, as evidenced by high-resolution TEM and circular dichroism.

A systematic resonance Raman study of DNA-SWNT complexes elucidated that the intensity of the ratio between the D-band and the G-band (I_D/I_G) depends on the nanotube length (Chou et al. 2007b). Also, an increase in the intensity is observed for several features of the intermediate frequency mode region of the Raman spectra of DNA-SWNTs, as the nanotube length decreased below the wavelength of light (Chou et al. 2007a). Raman spectroscopy was also used to show a strong dependence of the G-band of the spectra of the DNA-SWNTs on the relative humidity (Kawamoto et al., 2006b). On the other hand, the relationship between the optical properties of DNA-SWNT complexes and their length was studied and it was shown that as the nanotube length increases, the intensity for the
absorption, near-infrared fluorescence and Raman scattering features of the samples are enhanced (Fagan et al. 2007a). Alternatively, a study by Kawamoto and coworkers demonstrated that the asymmetric profile of the Breit-Weign-Fano (BWF) Raman line disappears when HiPco SWNTs are individually dispersed due to DNA wrapping around the SWNTs (Kawamoto et al., 2006c), which suggests that the asymmetric feature of the BWF line can be attributed to bundling effects in SWNTs dispersions. Another study by this group revealed that the asymmetric feature of the BWF Raman line reappears when the DNA-SWNTs dispersion is dried in air, and demonstrated the reversibility of the changes in the BWF line by switching between the air-dried and hydrated states of the DNA-SWNTs dispersions (Kawamoto et al., 2006a).

Several groups have also studied the stability of the DNA-CNT complexes. For instance, it has been demonstrated that DNA-SWNTs prepared with double-stranded DNA are very stable after one month of storage, even when free double-stranded DNA was removed from the dispersion (Noguchi et al., 2008). The stability of different dispersions of DNA-SWNTs was also tested by heating the dispersions and following the flocculation process via UV-visible spectroscopy (Vogel et al., 2007a; Vogel et al., 2007b). The thermal denaturation experiments demonstrated that the stability of the DNA-SWNT complexes increases with the length of the oligonucleotide used, since longer DNA chains can engage in a larger number of multivalent interactions. On the other hand, a study on the effect of UV irradiation on DNA-wrapped SWNTs showed that nanotubes wrapped with (GT)$_{15}$ are more stable under UV irradiation than CNTs wrapped with (T)$_{15}$ (Yoon et al., 2008).

Studies on the electrical properties of the DNA-wrapped CNTs have also been reported in the past few years. Hembram and Rao studied the electrical properties of DNA/MWNTs composites by modifying alumina substrates with dispersions of DNA/MWNTs with equal DNA concentration, but varying CNT composition, and by analyzing them by electrochemical impedance spectroscopy (EIS) (Hembram & Rao, 2009). The electrochemical results revealed that the charge transfer resistance of the system decreases (i.e. higher conductivity) with increases in CNT concentrations. This enhancement in conductivity was attributed to an increase in the conducting path due to the increase in the amount of CNTs, as evidenced by SEM. Alternatively, differences in the conductivity type of the nanotubes were reported after functionalization with DNA. Fantini and coworkers performed Raman and optical absorption measurements to demonstrate that an enrichment of semiconducting versus metallic nanotubes occurs when the nanotubes are dispersed with DNA instead of with sodium dodecyl sulfate (Fantini et al., 2007).

An SWNT field effect transistor (FET) with a DNA-wrapped SWNTs, was fabricated in order to study the effect of DNA wrapping on the electronic transport characteristics of SWNTs (Hwang et al., 2008). This report showed that after DNA wrapping, the conduction type of SWNTs was changed from p-type to n-type, and that the charge transport occurred through both the DNA and SWNT in the fabricated FET. Subsequently, the transition between a metallic SWNT to a semiconductor due to DNA wrapping around the nanotube, was demonstrated by FET-type measurements (Cha et al., 2009).

UV-visible spectroscopy has been used to monitor the electron transfer resistance between small molecule redox agents and DNA-wrapped nanotubes and to determine that there is a facile electron transfer between the redox reagents studied and the semiconducting CNTs (Zheng & Diner, 2004). For example, KMnO$_4$ and K$_2$IrCl$_6$ can oxidize the nanotubes, whereas NaBH$_4$ and Na$_2$SO$_4$ can reduce them. Furthermore, Xu and colleagues showed that
the redox chemistry of DNA-wrapped SWNTs with H$_2$O$_2$ depends on whether or not the suspension was purified by chromatography, since the purified DNA-SWNTs suspensions appeared to be less sensitive to hydrogen peroxide (Xu et al., 2008).

Electrochemical methods were employed to report the first-time electrocatalytic oxidation of DNA-wrapped CNTs in solution in the presence of Ru(bpy)$_3^{2+}$ (Napier et al., 2005). Conversely, absorption spectroscopy was used to study the donor-acceptor complex formed by Ag$^+$ and DNA-CNTs, and the results demonstrated the capability of the DNA-CNT complexes to catalyze the photosynthesis of Ag nanoparticles (Zheng & Rostovtsev, 2006).

Additional properties, ranging from pH dependence to cytotoxicity, have been studied by spectroscopic and microscopic techniques. Kelley and coworkers reported that the optical transitions of DNA-wrapped semiconducting nanotubes are dependent on pH (Kelly et al., 2005). Variations in pH have been used to control the aggregation of DNA-SWNTs (Han et al., 2008). At low pH values, the DNA-SWNTs dispersion aggregated, whereas at higher pH values, the aggregates disappeared and a clear dispersion was obtained.

Polarized photoluminescence measurements on DNA-SWNT complexes demonstrated that differences in magnetism exist among SWNTs chiralities (Torrens et al., 2007), whereas optical absorption spectroscopy served to report that anisotropic hypochromicity is observed for the optical transitions of DNA bases interacting with SWNTs (Hughes et al., 2007). On the other hand, the cytotoxicity of SWNTs suspended in different surfactants was studied by phase contrast light microscopy and absorbance spectroscopy, and the measurements demonstrated that while SWNTs dispersed with sodium dodecyl sulfate and sodium dodecylbenzene sulfonate were toxic to human astrocytoma cells, DNA-wrapped SWNTs did not affect the proliferation and viability of the cells (Dong et al., 2008).

### 3.3 Theoretical and simulation experiments

Theoretical and simulation experiments have been crucial to the understanding of the non-covalent interaction between DNA and CNTs, and to the elucidation of the structure of DNA-wrapped CNTs. The first theoretical report on DNA-wrapped CNTs was published in 2003 (Zheng et al., 2003a). Their simulations showed that short ssDNA strands (i.e. poly (T)) can bind to the surface of a (10,0) carbon nanotube in several allowed configurations, including helical wrapping with right- and left-handed turns, or surface adsorption with a linearly extended structure. Furthermore, the thermodynamics of binding of DNA to CNTs were estimated by comparing the minimized energy of the DNA-CNT complex with that of the DNA strand and the individual CNT. Their calculations demonstrated that the binding energy of ssDNA onto the surface of CNTs could compete effectively with the tendency of CNTs to aggregate and form bundles in order to maximize the interaction with each other.

Molecular dynamic simulations were subsequently performed on both DNA adsorption on the nanotubes walls and encapsulation inside the CNTs (Gao & Kong, 2004). It was determined that due to van der Waals forces between the DNA and CNTs, the DNA strands could be encapsulated inside or wrapped around the CNTs. The effect of nanotube size, temperature, DNA sequence and CNT-end group on the functionalization process was also studied. Conversely, Ranjan and coworkers performed density functional theory calculations of poly (T) and poly (CT) with CNTs, to show that no covalent interaction exists between the DNA and the CNTs, but long-range van der Waals interactions are the main force (Ranjan et al., 2005).
Computer simulations were used by Gladchenko and coworkers to study the binding between short fragmented double stranded DNA and CNTs (Gladchenko et al., 2006). The results revealed that approximately 60% of the bases are out of the stacking with the nanotubes. Their model suggests that the denatured parts of the double stranded DNA wrap around the CNTs, whereas no stacking interaction was found between the double-stranded portion of the DNA and the CNT.

Manohar and coworkers used scaling arguments and molecular dynamics to study the factors that contribute to the formation of the DNA-CNT hybrids (Manohar et al., 2007). The results suggest that a fraction of the bases unstuck from the CNT, and that at low ionic strength, the main forces contributing to the free energy are the adhesion between the bases and the CNT and electrostatic repulsion due to the charged phosphate groups in the DNA. The differences in adsorption of a 12-base pairs DNA fragment on uncharged, positively- and negatively-charged SWNTs was also studied (Zhao & Johnson, 2007). The simulations demonstrated that DNA can bind to the surface of uncharged or positively charged SWNTs, whereas DNA does not adsorb on negatively charged SWNTs. Furthermore, the results showed that the hydrophobic end groups of DNA are attracted to the hydrophobic SWNT surface, while the hydrophilic backbone does not bind to the nanotube.

Atomistic molecular dynamic simulations on DNA and CNTs were used to determine that the presence of SWNTs induces a conformational change in DNA in order to enable the wrapping of DNA around SWNTs with right- and left-handed helices, achiral loops and disordered, kinked structures (Johnson et al., 2008). These results also demonstrated that purines exhibit the strongest binding towards nanotubes, and that this binding occurs via the n-n stacking interaction between DNA bases and the nanotubes sidewalls. On the other hand, Stepanian and coworkers used both ab initio MP2 (second order Møller-Plesset perturbation theory) and DFT (density functional theory) methods to study the stacking interaction of cytosine and to determine that the interaction energy of the DNA-CNT complex formed is < 42.4 kJ/mol (Stepanian et al., 2008).

Shtogun and coworkers used DFT to study the interactions between DNA bases and their radicals with the nanotube surface (Shtogun et al., 2007). Their studies suggest that both DNA bases and their radicals can be easily adsorbed on nanotube surfaces due to the non-covalent interaction between the delocalized π orbitals from the DNA and the nanotubes. DFT was also used to study the adsorption of nucleic bases on nanotubes of small diameter (Gowtham et al., 2008). The calculated binding energies followed the hierarchy G>A>T>C>U and the molecular polarizability dominated the interaction between the bases and the nanotubes. Alternatively, Das and coworkers used the ab initio Hartree-Fock method to study the binding of DNA bases to CNTs with and without considering the solvation effects of water (Das et al., 2008). By including solvation energy, the relative binding energy preference changes from G>A>T>C to G>T>A>C, which was in good agreement to their experimental results. The same order of binding preference in gas-phase was reported by DFT in another study (Wang et al., 2008). Nevertheless, it was also found that for aqueous solutions, the binding preference varies from A>G>T>C for (10,0) SWNTs to G>A>T>C for (5,5) SWNTs, showing that cross-stacking has a weak dependence on the nanotube diameter. Even though theoretical studies have given us a better understanding of the type of forces and interactions involved on DNA-wrapping around CNTs, there are still many unanswered questions, as well as some discrepancies on the data reported. Additional studies that can consider environmental conditions such as solvent effects and ionic strength.
could provide a clearer picture of the interactions between DNA and CNTs. Furthermore, it is very difficult to obtain data that can be universally applied to all types of DNA-CNT complexes, because of the many possible permutations due to the different DNA sequences, DNA lengths, and types of CNTs (e.g. metallic, semiconducting, chiral, etc.) available.

3.3 Assembly on solid substrates
The development of a straightforward methodology for the ordered assembly of CNTs on solid substrates is a very desirable goal, because it would facilitate the use of CNTs as sensors, and at the same time, it would make easier the study of CNTs by surface techniques such as XPS, SEM, and ellipsometry, among others. Individually dispersed DNA-wrapped CNTs have been assembled and characterized on solid substrates, and have also been proposed for biosensing applications. These DNA-CNT complexes have been deposited as a film on substrates such as glassy carbon (Li et al., 2007), glass (Hu et al., 2005), and gold (Zangmeister et al., 2007), aligned on a SiO$_2$ surface with a gold boundary (Mclean et al., 2006), and as self-assembled monolayers (SAMs) on gold electrodes (Sánchez-Pomales et al., 2005; Sánchez-Pomales et al., 2006; Sánchez-Pomales et al, 2007b; Sánchez-Pomales & Cabrera, 2007).

Hu and coworkers prepared an electrode with DNA-wrapped CNTs (Fig. 3) by depositing the DNA-CNTs complexes onto a glass substrate (Hu et al., 2005). The individually dispersed DNA-CNTs adhered tightly to the substrate and formed a uniform, stable film, which was subsequently used for the electrochemical detection of dopamine. SEM analysis of the electrode confirmed that the DNA-CNTs were well dispersed in the film, and had an average length of 600 nm. FT-IR and EDS were also used to verify the presence of the DNA-wrapped CNTs on the glass surface. Conversely, electrochemical analysis revealed that the DNA-CNTs modified electrode possessed a wide and flat potential window and fast electron transfer for the Fe$^{3+/2+}$ redox couple, which are advantages for electrodes used in typical electrochemical detection applications. On a subsequent report, the properties of the DNA-CNTs film were compared versus those of an electrode prepared with oxidized MWNTs (Hu et al., 2007). This study showed that even though the oxidized MWNTs exhibited a wider potential window with lower background current in KCl, higher peak currents and smaller difference of peak potentials in Fe(CN)$_6^{3-/4-}$, the film made with the DNA-CNTs performed better in the detection of low concentration of dopamine in the presence of excess ascorbic acid.

Zangmeister and coworkers investigated the adsorption properties of DNA-wrapped CNTs on bare gold and on self-assembled monolayers of neutral, positively and negatively charged species (Zangmeister et al., 2007). X-ray photoelectron spectroscopy (XPS), reflection absorption infrared spectroscopy (RAIRS) and Raman spectroscopy results demonstrated that the DNA-CNT complexes adsorb preferentially to positively charged amine-terminated SAMs or to bare gold, in comparison to neutral methyl-terminated or negatively charged carboxylate terminated SAMs. Their results suggest that electrostatic interactions between the negatively charged phosphate groups of the DNA and the charge of the species on the Au surface influence the adsorption of the DNA-wrapped CNTs.
DNA lengths, and types of CNTs (e.g. metallic, semiconducting, chiral, etc.) available.

3.3 Assembly on solid substrates

Fig. 3. Schematic showing the fabrication process used by Hu et al. to modify the glass substrate with DNA-wrapped SWNTs (left) and SEM image showing the topography of the modified electrode (right). Reprinted with permission from (Hu et al., 2005). Copyright (2005) American Chemical Society.

Glassy carbon electrodes were modified with either DNA partly-wrapped SWNTs (DNA-p-SWNTs) or DNA fully-wrapped SWNTs (DNA-f-SWNTs) by H. H. Li and coworkers (Li et al., 2007). The DNA-p-SWNTs were separated from DNA-f-SWNTs and from free DNA by differential centrifugation. The modified electrodes were characterized by SEM and cyclic voltammetry in Fe$^{3+/2+}$, and the results showed that the DNA-p-SWNTs form a uniform and porous film, which displays better electrochemical properties that the DNA-f-SWNTs.

DNA-wrapped SWNTs have also been deposited on silicon wafers and mica substrates (Hopkins et al., 2007). Alignment and organization of the DNA-CNT complexes was achieved by using an inkjet printer for the deposition of the DNA-SWNTs, and characterization of the modified substrates was performed by SEM and AFM. Mclean and coworkers studied the deposition of dilute solutions of DNA-wrapped CNTs on SiO$_2$ and they showed that the adsorption of the DNA-CNT complexes on SiO$_2$ is dependent on pH, and at pH values >5 ($pK_a$=5), the DNA-CNTs do not adsorb on the substrate, whereas at pH values <5, DNA-CNTs were adsorbed with random orientations (Mclean et al., 2006). However, if the SiO$_2$ substrate was coated with a hydrophobic layer, adsorption of the DNA-CNTs occurred over a broad pH range, and the complexes were aligned parallel to each other. The results showed that the thickness of the hydrophobic layer influenced the alignment of the DNA-CNTs, and for chains with $C_2$ and $C_6$ alignment was observed, whereas the adsorption was random for $C_{18}$. Additionally, they studied the factors that affect the DNA-CNT complexes adsorption rate and they reported that longer incubation times, lower pH and higher ionic strength increase the adsorption rate onto the modified SiO$_2$ substrate. Deposition experiments with patterned metal electrodes on the SiO$_2$ surface were also performed, and it was found that the metal boundary tends to impose a local orientation on the CNTs.

Alignment of DNA-CNT complexes was also observed by Gigliotti and coworkers (Gigliotti et al., 2006). Their AFM results demonstrated that high density arrays of aligned DNA-CNT complexes, produced by long genomic ss-DNA, could be formed at the edges of air-drying droplets on aminopropyltriethoxysilane (APTES)-terminated silicon substrates. Alternatively, deposition and meniscus alignment of DNA-CNT complexes was performed on a silicon wafer coated with an alkyl-silane monolayer, and the effects of pH, ionic strength and time on the density of the deposited DNA-CNTs were studied (Khripin et al., 2009a). Electrochemical oxidative polymerization of ethylenedioxythiophene (EDOT) was used by Bae and coworkers to deposit complexes of ds-DNA-CNTs on indium tin oxide (ITO)
electrodes (Bae et al., 2004). Their results revealed that the DNA-CNT complexes possessed a fibrous morphology, and that the ability of DNA to bind an intercalator (i.e. ethidium bromide) was retained.

Alternating current dielectrophoresis has also been used to deposit DNA-SWNTs across Au electrodes (Tallin et al., 2004). The results showed that debris-free individual SWNTs were bridging the electrodes when DNA-SWNTs complexes were used, whereas when SWNTs dispersed with a surfactant were deposited, carbon debris was attached to the SWNTs, and that there was a tendency towards nanotube aggregation into bundles. On the other hand, a study by Karachevtsev et al. revealed that after a film of DNA-SWNTs dried over a Si substrate, the SWNTs aggregated, as evidenced by an increase in the Raman G' peak intensity, and a broadening of the G' peak (Karachevtsev et al., 2006b).

Fibers of DNA/SWNTs/poly(ethylene oxide) with an average diameter of 150 nm were electrospun on Pt-coated glass slides, as confirmed by Raman spectroscopy and SEM (Liu et al., 2008). The fibers showed improved electroactive behavior and demonstrated their capability as an immobilization matrix for a glucose oxidase biosensor. Electrochemical deposition was used to immobilize DNA-CNT composites on glassy carbon electrodes (Li et al., 2008). The modified electrodes exhibited good stability, and the DNA-CNT composites showed good electrocatalytic activity towards the detection of biomolecules such as dopamine, uric acid and ascorbic acid.

DNA-SWNTs were also deposited over an n-octadecyl mercaptaon monolayer on Au, and the modified electrode was studied by cyclic voltammetry and electrochemical impedance spectroscopy (Zheng et al., 2009). Furthermore, the release of the DNA-SWNTs from the solid/liquid interface was controlled by applying either a positive (0.90 V vs. Ag | AgCl) or a negative (-1.40 V vs. Ag | AgCl) potential.

DNA-SWNT complexes were also immobilized on gold via the formation of mixed self-assembled monolayers (Fig. 4), and our group was the first to report that the DNA-SWNTs were attached in a perpendicular fashion to the gold electrodes (Sánchez-Pomales et al., 2005; Sánchez-Pomales et al., 2006). Such unusual attachment geometry was, up to that time, obtained only by direct growth of the CNTs on a surface by chemical deposition or by post-synthesis attachment of oxidized/activated CNTs by covalent means on previously formed self-assembled monolayers. The developed methodology represents a straightforward alternative to the assembly of aligned CNTs on solid surfaces, and it offers the advantage of allowing the tailoring of the surface by controlling simple parameters such as concentration and modification time, among others. The efficiency of the immobilization process was determined by microscopic, electrochemical, and spectroscopic techniques. Mixed self-assembled monolayers, containing aggregates of DNA-SWNT hybrids with diverse surface coverage were obtained (Sánchez-Pomales & Cabrera 2007). Our group was able to tailor the surface coverage by varying the initial concentration of DNA-SWNTs or by using reductive electrochemical desorption (Sánchez-Pomales et al., 2006; Sánchez-Pomales & Cabrera 2007). The results revealed that the use of DNA-SWNT hybrids to form SAMs on gold provides advantages over traditional DNA SAMs (Sánchez-Pomales et al., 2007b). Additionally, vertically aligned SAMs of DNA-SWNTs on gold, prepared by Viswanathan and coworkers, were subsequently coated with polyaniline, modified with acetylcholinesterase and used as a biosensor for the detection of pesticides such as methyl parathion and chlorpyrifos (Viswanathan et al., 2009).  

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vertically aligned SAMs of DNA-SWNTs on gold, prepared by Viswanathan and coworkers, advantages over traditional DNA SAMs (Sánchez-Pomales et al., 2007b). Additionally, the results revealed that the use of DNA-SWNT hybrids to form SAMs on gold provides electrochemical desorption (Sánchez-Pomales et al., 2006; Sánchez-Pomales & Cabrera 2007). Surface coverage by varying the initial concentration of DNA-SWNTs or by using reductive assembled monolayers, containing aggregates of DNA-SWNT hybrids with diverse surface determined by microscopic, electrochemical, and spectroscopic techniques. Mixed self-assembled monolayers. The developed methodology represents a straightforward synthesis attachment of oxidized/activated CNTs by covalent means on previously formed substrate, the SWNTs aggregated, as evidenced by an increase in the Raman G peak (Karachevtsev et al., 2006b). On the other hand, a fibrous morphology, and that the ability of DNA to bind an intercalator (i.e. ethidium bromide) was studied in the next sections. Fig. 4. Schematic representation of the functionalization and DNA-mediated attachment of carbon nanotubes on gold. (The figure does not necessarily represent the correct ratio between the species chemisorbed on the gold surface, and the drawings are not to scale.)

3.4 Applications
Since the first reports on the synthesis of DNA-wrapped CNTs, the amount of scientific articles on the application of these hybrids has increased exponentially. The DNA-CNT supramolecular complexes have been proposed for applications ranging from biological transporters and biosensors (Sánchez-Pomales et al., 2009) to fibers for artificial muscles (Shin et al., 2008) and bioelectrodes for fuel cells (Lee et al., 2010; Sánchez-Pomales et al., unpublished b). Furthermore, the use of DNA-wrapped CNTs has helped in the purification and separation of CNTs by techniques as diverse as electrophoresis, size-exclusion chromatography and ultracentrifugation, among others. The main findings of these reports will be discussed in the next sections.

3.4.1 Chemical biosensors
DNA-wrapped CNTs have been used as biosensors for the detection of diverse species, including glucose (Karachevtsev et al., 2007; Xu et al., 2007), peroxide (Liang et al., 2007; Xu et al., 2007), dopamine (Ma et al., 2006; Hu et al., 2005), pesticides (Viswanathan, et al., 2009), vapors (Johnson et al., 2006), proteins (Wu et al., 2009), and ions (Heller et al., 2006; Jin et al., 2007), among others. Hu and coworkers reported the first application of DNA-wrapped SWNTs for biosensing (Hu et al., 2005). DNA-wrapped CNTs deposited over glass substrates were used as an electrochemical biosensor for the detection of dopamine. Their results showed that the prepared dopamine biosensor possesses excellent selectivity and sensitivity, even in the presence of interferences such as ascorbic acid. Additionally, the reported detection limit was low, demonstrating that the DNA-SWNTs-modified electrode can be used as an analytical dopamine biosensor. Dopamine was also detected by He’s group by using DNA-wrapped SWNTs in a self-doped polyaniline nanocomposite (Ma et al., 2006; Ali et al., 2007; Cheung et al., 2009). The biosensing capability of the DNA-SWNT/polyaniline composite was tested, and concentrations as low as 1 nM of dopamine were detected, with a linear range from 1 nM to 10 nM.
Non-covalent functionalization of DNA-wrapped SWNTs with glucose oxidase (GOx) was performed with the purpose of using DNA as an interface between the enzyme and the nanotubes, so that the enzyme retains its native structure and activity (Karachevtsev et al., 2007). Micromolar concentrations of glucose were detected by monitoring the changes in the near infrared (NIR) luminescence intensity of the GOx-DNA-SWNT complexes upon addition of glucose in the presence of potassium ferricyanide. The emission of the SWNTs was quenched by potassium ferricyanide, and it was subsequently restored after adding glucose. The possible application of DNA-wrapped SWNTs for glucose and peroxide biosensors was studied by Zhao’s group (Xu et al., 2007; Tu et al., 2007). DNA SWNT hybrids were allowed to interact with glucose, in the presence of glucose oxidase and peroxide, and decreases in the intensity of the S_{11} band of the absorption spectra of the hybrids were recorded. Peroxide was detected by electrochemical means with a DNA-wrapped SWNTs biosensor (Fig. 5) in the presence of hemoglobin (Hb) (Liang et al., 2007). Hb/ssDNA-SWNTs films were analyzed by cyclic voltammetry in buffer in the presence of H_{2}O_{2} and it was shown that the peroxidase activity of Hb was preserved in the films. These results show that DNA-SWNT hybrids may be successfully used as peroxide and glucose analytical biosensors, and might find applications in the chemical, clinical and biological areas, among others (Xu et al., 2007).

Fig. 5. Schematic showing the peroxide biosensor prepared with DNA-SWNTs complexes. Reprinted with permission from (Liang et al., 2007). Copyright (2007) by MDPI.

DNA-CNT complexes have also been used for the detection of gas odors, including methanol, propionic acid, trimethylamine (TMA), dinitrotoluene (DNT) and dimethyl methylphosphonate (DMMP) (Johnson et al., 2006; Staii et al., 2005; Poonam & Deo, 2008). A field effect transistor (FET) device based on a DNA-CNT complex was used to detect five different odors that a bare CNT FET device was not able to detect. The device’s response was enhanced by adding DNA, due to an increase in the binding affinity of the DNA layer towards the analytes. The device showed good sensor response (which was specific to the base sequence used), low recovery times and excellent reproducibility for repeated measurements with a single device and among different devices.

Reports by several groups have elucidated the potential of DNA-SWNT hybrids for ion detection. For example, Strano’s group studied the decrease in the NIR emission energy of the DNA-wrapped nanotubes produced when divalent metal cations, which stabilize the Z form of DNA, induced a conformation change of the DNA adsorbed on the nanotube surface (Heller et al., 2006; Jin et al., 2007). A shift in band gap was observed in the emission
and absorption spectra, and an ion sensitivity of Hg$^{2+}$ > Co$^{2+}$ > Ca$^{2+}$ > Mg$^{2+}$ was reported. Furthermore, mercuric ions were detected in whole blood, black ink, and cells and tissues, which suggest that the DNA-wrapped SWNTs can be used as novel probes in biological media. Conversely, Gao and coworkers detected trace levels of mercuric ions in aqueous solutions containing DNA-wrapped SWNTs, by monitoring the decrease in the induced circular dichroism signal of the DNA-SWNTs produced by the increase of DNA pitch that occurs when the mercuric ions bind to DNA (Gao et al., 2008). Additionally, tin and arsenic ions have been detected by electrochemical means by using electrodes modified with the DNA-nanotube complexes (Liu & Wei, 2008; Ferancová et al., 2007).

### 3.4.2 DNA hybridization biosensors

Several groups have studied the hybridization event between a DNA-wrapped CNT and a free complementary DNA strand. Nevertheless, there are discrepancies between the different groups on whether hybridization occurs on the nanotube surface or whether the nanotube is displaced once the DNA strands hybridize. Cheng and Zhang reported that delamination of DNA and precipitation of the nanotube occur when a complementary DNA sequence, free in solution, is allowed to interact with a DNA-wrapped CNT complex, as evidenced by a visual test, UV-visible spectroscopy, and gel electrophoresis (Chen & Zhang, 2006). Tan’s group has also provided evidence that shows that the hybridization event occurs in solution rather than on the nanotube surface (Yang et al., 2008a; Yang et al., 2008b). For their studies, they have used DNA probes labeled with dyes to demonstrate that the fluorescence of the dye is quenched in the DNA-SWNT complex due to the proximity of the dye to the nanotube surface, but the fluorescence is subsequently restored when a complementary DNA strand is added to the system. Fluorescence anisotropy data and fluorescence intensity results obtained after the system was dialyzed were used to support the hypothesis that DNA hybridization does not occur on the nanotube surface. Label-free DNA strands (both linear and hairpin structures) have been successfully used by the same group to detect hybridization between DNA-SWNT complexes and the complementary DNA strands in the presence of a solution ethidium bromide, a DNA-intercalating dye (Liu et al., 2009).

The opposite theory has been supported by Stano’s, Baik’s and Cabrera’s groups. Strano’s group reported that hybridization between a target DNA sequence and the complementary probe sequence that was wrapped around a SWNT occurs on the nanotube surface (Jeng et al., 2006). The hybridization event was detected by using the optical modulation of the NIR fluorescence of the SWNTs. An energy shift in the fluorescent peak of DNA-SWNTs that occurred upon addition of the complementary DNA strand, and not when a non-complementary sequence was used, was attributed to a denser surface coverage of DNA in the SWNT surface after hybridization. Forster resonance energy transfer (FRET) between the fluorescent labeled DNA strands was used to corroborate hybridization at the SWNTs surface, and by using the optical modulation of the SWNTs NIR fluorescence, a detection limit of target DNA in the nanomolar range was obtained. On a subsequent report, Strano’s group compared the kinetics of DNA hybridization at DNA-SWNTs complexes versus free DNA, and the data showed that the kinetics of DNA hybridization at DNA-SWNT complexes is slower than the kinetics in free DNA solution, with both entropic and activation energy barriers higher for DNA-SWNTs in comparison to free DNA (Jeng et al., 2007). A two-step model, which includes a first step where free, target DNA strands are...
adsorbed to the DNA-SWNTs probes, followed by a second slower hybridization step was proposed. Balić’s group, on the other hand, studied the hybridization event at the nanotube surface by monitoring the changes in the absorption spectra of DNA-wrapped SWNTs (Cao et al., 2008). Furthermore, Cabrera’s group provided microscopy, electrochemical and spectroscopic evidence that demonstrated that the hybridization event between SAMs of the complementary DNA sequence and DNA-CNT complexes occurs on the surface of the DNA-CNT, and that therefore, the nanotubes can be deposited on gold surfaces previously modified with a DNA SAMs (Sánchez-Pomales et al., unpublished a).

Instead of performing hybridization on the surface of DNA-SWNTs complexes, Huang and coworkers used a DNA complex containing both a single-stranded and a double-stranded portion to functionalize SWNTs, and they were able to detect a particular DNA sequence within a complex genome (Hwang et al., 2006). The single-stranded part of the DNA was preferentially bound to the SWNTs, whereas the double-stranded (ds) portion was freely exposed on the exterior. Denaturation of the ds portion was achieved by heating, and the now exposed ss-probe sequence was allowed to hybridize with target genomic, as evidenced by a southern blotting employing Raman spectroscopy.

Field effect transistors (FETs) made with DNA-wrapped CNTs have been used to detect specific nucleic acid sequences (Onoa et al., 2006; Tang et al., 2006). The functionalization of CNTs with DNA facilitates the placement of highly purified nanotubes on the devices, and the DNA strands can be subsequently removed from the nanotube by thermal denaturation, if desired (Onoa et al., 2006). Nevertheless, these reports showed that the presence of DNA on the nanotube surface does not alter significantly the carrier transport properties of CNTs.

### 3.4.3 Biological transporters

Studies by different groups have established the capabilities of DNA-wrapped CNTs as cellular transporters, due to the higher biostability of these complexes in comparison with free DNA strands. Wu and coworkers reported that DNA probes bound to SWNTs are protected from nuclease digestion and from interference from DNA binding proteins (Wu et al., 2008). These protected DNA probes, which target mRNA inside the cells, possess increased intracellular biostability and enhanced self-delivery capabilities, providing significant advantages over free DNA probes.

Dai’s group, on the other hand, demonstrated the potential of DNA-wrapped CNTs as intracellular transporters for DNA, and showed that DNA-wrapped CNTs are capable of transporting oligonucleotides into living cells via an energy-dependent endocytosis mechanism (Kam & Dai, 2005a; Kam et al., 2007). In another study by the same group, it was revealed that short NIR laser pulses can be used to release DNA cargoes from SWNTs, and that the released oligonucleotides can translocate into the cell nucleus (Kam et al., 2005b).

Alternatively, continuous NIR will cause extensive local heating of the SWNTs and will induce cell death. Selective cancer cells destruction was reported for SWNTs functionalized with a folate moiety, demonstrating their capabilities for drug delivery and cancer therapy.

### 3.4.4 Purification and separation

Dispersion of carbon nanotubes by DNA also has the benefit of purifying the nanotubes (Taeger et al., 2004; Sánchez-Pomales et al., 2007a; Tu & Zheng, 2008) and of opening the door for separation applications as previously reviewed (Tu and Zheng, 2008).
Increased intracellular biostability and enhanced self-delivery capabilities, providing al. (2008). These protected DNA probes, which target mRNA inside the cells, possess Studies by different groups have established the capabilities of DNA-wrapped CNTs as on the nanotube surface does not alter significantly the carrier transport properties of CNTs. Nevertheless, these reports showed that the presence of DNA the DNA strands can be subsequently removed from the nanotube by thermal denaturation, CNTs with DNA facilitates the placement of highly purified nanotubes on the devices, and Field effect transistors (FETs) made with DNA-wrapped CNTs have been used to detect exposed on the exterior. Denaturation of the ds portion was achieved by heating, and the preferentially bound to the SWNTs, whereas the double-stranded (ds) portion was freely within a complex genome (Hwang et al., 2006). The single-stranded part of the DNA was Instead of performing hybridization on the surface of DNA-SWNTs complexes, Huang and (Taeger et al., 2004; Sánchez-Pomales et al., 2007a; Tu & Zheng, 2008) and of opening the Dispersion of carbon nanotubes by DNA also has the benefit of purifying the nanotubes Chromatographic techniques have been used to separate DNA-wrapped CNTs by conductivity type, diameter, chirality and length. Zheng’s group published the first report on the chromatographic separation of DNA-CNT complexes in 2003 (Zheng et al., 2003). Ion exchange chromatography was used to separate DNA-CNT complexes into fractions of different conductivity and length and even though the separation of the nanotubes into metallic and semiconducting tubes was convoluted by variations in length, this report served as the basis for additional efforts on the separation of nanotubes by chromatographic means (Strano et al., 2004; Zheng, 2004; Lustig et al., 2006). A subsequent paper by the same group revealed that, by using ion-exchange chromatography on the DNA-CNTs complexes, earlier fractions could be enriched in smaller diameter and metallic CNTs, whereas late fractions were enriched in larger diameter semiconducting CNTs (Zheng et al., 2003). Furthermore, size exclusion chromatography has been successfully used to separate DNA-wrapped CNTs by length (Huang et al., 2005; Bauer et al., 2007; Bauer et al., 2008), and a combination of size exclusion chromatography followed by ion exchange chromatography was used to separate the complexes by diameter, length, conductivity and chirality (Zhang et al., 2008) and to obtain fractions enriched in a single chirality SWNTs (Zheng & Semke, 2007). Additional separation of the nanotubes by length, diameter and conductivity has been achieved by several techniques, including flow-field flow fractionation (Chun et al., 2008), ultracentrifugation in aqueous density gradients (Arnold, et al. 2005), dielectrophoresis (Sickert et al., 2005), and agarose gel electrophoresis (Vetcher et al., 2006).

4. Summary and future prospects

Chemical functionalization of CNTs is currently one of the most efficient methods for increasing their solubility, for facilitating their use as standard chemical reagents and for combining their unique properties with those of other materials with interesting characteristics. Chemical functionalization of CNTs by DNA has drawn much attention in the past years, since DNA-CNT hybrids can take advantage of the unique properties of the nanotubes and the outstanding recognition capabilities of DNA. Particularly, non-covalent functionalization of CNTs by DNA wrapping is a relatively simple procedure that produces a distinct chemical entity in aqueous solution due to the strong non-covalent interaction between the DNA strands and the CNTs. Non-covalent functionalization of CNTs by DNA increases the solubility of the tubes in aqueous solution, and has the benefits of purifying the nanotubes, facilitating separation applications, and allowing further functionalization of CNTs without altering their unique properties.

DNA-CNT complexes are more manageable than as-received CNTs, and their assembly into different solid substrates has been reported. Additionally, the DNA strands have offered additional recognition capabilities to the system, and have therefore allowed the use of DNA-CNT complexes as sensors for biomolecules, ions and gases, as a biosensor for DNA hybridization, and as biological transporters. The optimization of the current methods available for the controllable integration of the DNA-CNT hybrids into solid substrates is a desirable goal, since it provides opportunities for additional applications of these complexes as sensors. For example, the modification of CNTs with DNA aptamers (Chen et al., 2009) and molecular beacons, and their application as ion, protein or DNA sensors are interesting potential areas of research. Furthermore, additional studies, both theoretical and experimental are needed in order to solve the current discrepancy on whether DNA
hybridization occurs on solution or on the tube surface. A clearer understanding of the interactions involved in the hybridization event with DNA-CNTs might allow the development of improved DNA hybridization sensors.

On the other hand, further studies of these DNA-CNT complexes must be performed in order to fully control the properties of the complexes and to exploit all of their possible uses and applications. Theoretical studies and simulations have provided us with a better understanding of the type of forces and interactions involved on DNA-wrapping around CNTs, but there are still numerous unanswered questions. Additional theoretical studies that can consider the effects of variations in DNA sequence and length, CNT type, and solvent conditions, among others, can enhance our knowledge of all the interactions involved during the functionalization process, and would allow us to finely tailor and control the DNA-CNT complexes depending on our needs.

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5. References


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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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