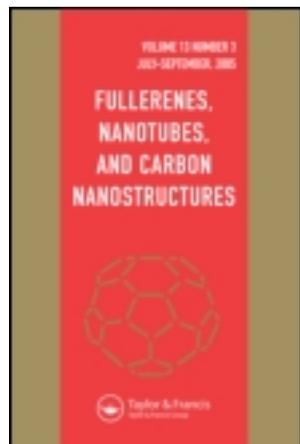


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Carbon Nanotubes: A Review of Chemistry Principles and Reactions

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Carbon Nanotubes: A Review of Chemistry Principles and Reactions

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Carbon nanotubes (CNTs) exhibit excellent mechanical, electrical and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make CNTs an ideal reinforcing agent. In this paper, discussions on structure, properties, covalent and noncovalent functionalization, and application of chemistry functionalized carbon nanotubes are included.

Keywords Carbon nanotubes, covalent fictionalization, covalent chemistry of CNTs

Introduction

Carbon nanotubes (CNTs), in both the single-walled (SWCNT) and multi-walled (MWCNT) forms, are widely considered to be the wonder materials of the 21st century and bring new paradigms to diverse fields, including electronics (1), structural integrity (2), biomedical engineering (3–5), tissue engineering (5), drug delivery (6), nanoinjectors (7), neuroengineering (8), gene therapy (9) and biosensor technology (10). Several reviews of CNTs regarding their methods of synthesis (11,12) and their superior mechanical, chemical and electrical properties exist in the literature (11,13,14). In this article, we focus on the attributes relevant for the practical application of CNTs in biomedicine. An example of the utility of CNTs in biomedicine is their relatively large length-to-diameter aspect ratio (which can exceed 106, with an average length of 1 mm and diameter about 1 nm) with a very large surface area, which makes CNTs amenable for high sensitivity molecular detection and recognition. Consequently, a large fraction of the CNT surface can be modified with functional groups of various complexities, which would modulate its in vivo and in vitro behavior. In spite of such attractive features, the toxicity of CNTs is a prime

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concern, with several groups pointing to their similarity to asbestos fibers (15). CNT toxicity in both in vivo and in vitro studies has been attributed to various factors, for instance, length, type of functionalization, concentration, duration of exposure, method of exposure and even the dispersant used to solubilize the nanotubes. Yet many studies suggest that such attributes for CNT toxicity are unfounded. These inconsistencies seem to arise largely due to differences in experimental protocol; whereas some points of view have been reconciled, most aspects of CNT toxicity remain uncertain. This review aims to synthesize and further analyze representative data on toxicity by first considering how CNTs are designed for biomedical purposes, how this process itself can promote toxicity and the behaviors of these CNTs when in clinical use, which all combine to explain the current toxicity profile of CNTs. A fresh evaluation of these studies yields new insight into CNT toxicity, with emphasis on issues such as cell specific tolerance, rates of toxic events, mechanism of cell injury and organ-specific bio distribution. In addition, we hope this review will stimulate further research into the fundamental aspects relevant for nanotube application, such as intrinsic defects, methods of synthesis, and nature of the functional group, all of which underlie biocompatibility issues and eventual widespread application.

Structure and Properties of Carbon Nanotubes

CNTs can be classified as SWCNTs and MWCNTs (Figure 1) (16). The structure of an individual SWCNT can be regarded as a two-dimensional (2-D) graphene sheet cut

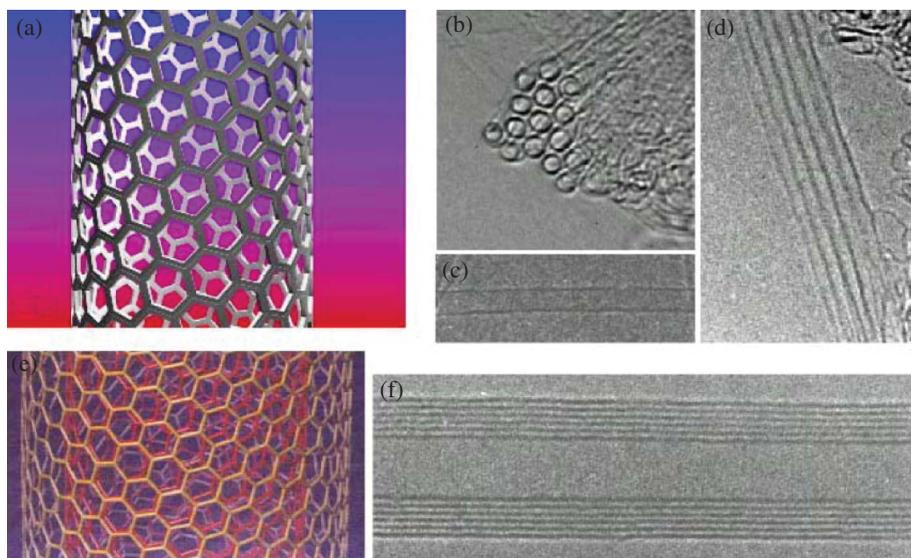


Figure 1. Structure of single-walled (SWCNT) (a–d) and multi-walled (MWCNT) carbon nanotubes (e,f). (a) Shows a schematic of an individual helical SWCNT; (b) shows a cross-sectional view (TEM image) of a bundle of SWCNTs [transverse view shown in (d)]. Each nanotube has a diameter of ≈ 1.4 nm, and the tube-tube distance in the bundles is 0.315 nm; (c) shows the high-resolution TEM micrograph of a 1.5 nm diameter SWCNT; (e) is the schematic of a MWCNT and (f) shows a high resolution TEM image of an individual MWCNT. The distance between horizontal fringes (layers of the tube) in (f) is 0.34 nm (close to the interlayer spacing in graphite) (color figure available online).

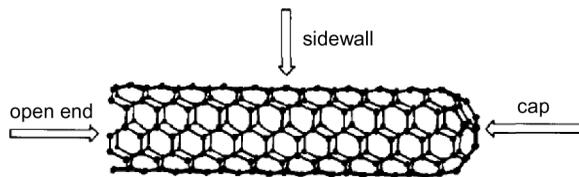


Figure 2. Structure of the single-walled carbon nanotube.

at various angles with respect to the hexagonal lattice that has been wrapped up into a seamless cylinder, which is capped by fullerene hemispheres at both ends (Figure 2) (17). MWCNTs are composed of concentric cylinders placed around a common central hollow, with spacing between the layers close to that of the interlayer distance in graphite (≈ 0.34 nm).

CNTs can be metallic or semiconducting, depending on their diameter and chirality. “Armchair” tubes have energy bands that cross the Fermi level and are therefore metallic. “Chiral” and “zigzag” nanotubes are expected to be metallic when $n-m = 3l$ (where l is an integer) or semiconducting with an energy gap of order about 1 eV when $n-m \neq 3l$. n and m are integers of the vector equation $R = na_1 + ma_2$, where a_1 and a_2 are the unit cell vectors of a graphen sheet. Figure 3 shows the electronic density of states (DOS) of a metallic and a semiconducting SWCNT close to Fermi level (18). For the metallic SWCNT, there is a finite value of the DOS at the Fermi level. On the other hand, a complete gap between the spikes close to Fermi level can be found in the semiconducting SWCNT. The energy separation between each pair of peaks represents the band gap of SWCNTs. By using simple tight-binding (STB) theory, in which the electronic band structure is assumed to arise from a pure p-orbital at each conjugated carbon atom, the low-energy band gap transitions take a simple analytical form: $S_{11} = 2a\beta/d$, $S_{22} = 4a\beta/d$, $M_{11} = 6a\beta/d$, where a is the carbon-carbon bond length (0.142 nm), β is the transfer or resonance integral between the p- and π -orbitals ($\beta = 2.9$ eV) and d is the diameter (nm) of the particular semiconducting or metallic SWCNT. S_{11} and S_{22} are the first and second pairs of singularities in the DOS of

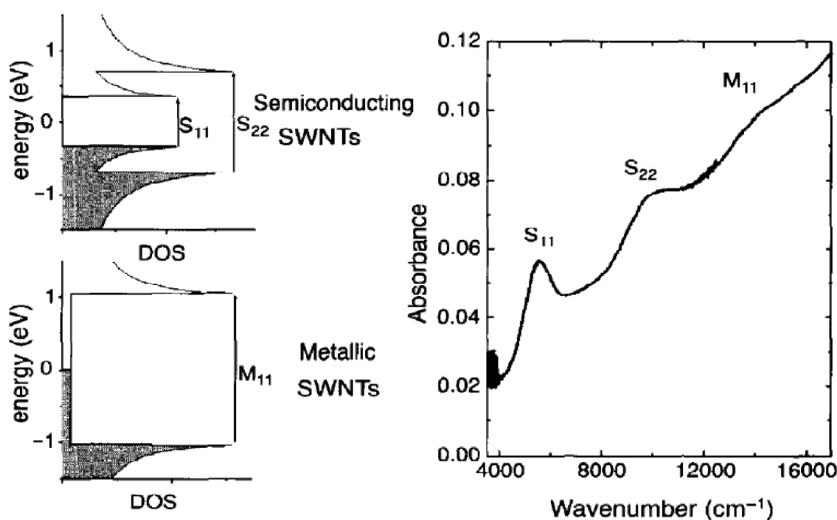


Figure 3. Interband transition of arc-produced SWCNTs near Fermi level.

semiconducting SWCNTs, respectively. M_{11} corresponds to the transition between the first pair of singularities in the DOS of metallic SWCNTs (17–21). The characteristic interband electronic transitions provide the spectroscopic signature of the SWCNTs in the near-IR (NIR) VIS spectral region (Figure 3).

As most SWCNT preparations are a mixture of metallic and semiconducting SWCNTs, the interband transitions arising from both species are visible. Besides these unique electronic properties, CNTs exhibit excellent mechanical and thermal properties. CNTs exhibit the highest Young's modulus and tensile strength of all known materials. The Young's modulus for an individual (10, 10) SWCNT is ≈ 0.64 TPa (20) and up to 1.47 TPa for a 15-SWCNT rope (21), which is much higher than that of conventional carbon fibers with values in the range of 200–800 GP (22). Young's modulus of MWCNTs is reported to be 1–2 TP (23), and the bending strength of individual MWCNTs reaches 28.5 GP (24). The measured thermal conductivity of an individual MWCNT (about 3000 W/m²K) is larger than that of natural diamond and the basal plane of graphite (both 2000 W/m²K).

Chemistry of Carbon Nanotubes

The covalent chemistry of CNTs may be classified into two categories (25). The first involves functionalization at the ends or at defect sites of the CNTs, where there exists the possibility to add to the carbon nanotube at an abounded site without attacking the π -system; this type of chemistry usually involves reaction at a previously introduced carboxylic acid group. These carboxylic acid groups are usually generated by nitric acid treatment and can be used as precursors in functionalizations such as amidation and esterification (25–27). The second type of covalent chemistry involves sidewall functionalization in which the carbon-carbon double bonds on the sidewall of CNTs react. Such reactions include fluorination (28), carbene (27–30) or nitrene addition, Birch (25,31), 1, 3-dipolar addition (32) and reactions with radical (33–35).

Covalent Functionalization

Oxidation of Carbon Nanotubes

Oxidative processes were among the first chemical reactions to be applied to CNTs (33), mainly for the purposes of purification and catalyst removal. Heating of CNTs in air at 700°C for 10 minutes leads to the opening of the hemispherical end caps of CNTs and demonstrates the different reactivities of the bonds in CNTs (end cap vs. sidewall). The controlled annealing of SWCNTs in O₂ is an effective method of purification (35–37). Other gas-phase oxidation methods, including the use of H₂S + O₂ (34) and O₃ (38), have been reported. Liquid-phase oxidation processes, such as treatment with HNO₃ (38–40), HNO₃+H₂SO₄ (26,40), H₂SO₄ +KMnO₄ (41) and KMnO₄ (40), have been widely used in the processing of CNTs. These oxidants can remove the end caps of CNTs and introduce functional groups, such as COOH, -OH and -C=O, at the dangling bonds (40,42). Among these functionalities, the carboxylic acid group is of great importance, as it has been employed in a large number of CNT functionalization reactions. After nitric acid treatment of SWCNTs, the concentration of carboxylic acid groups is about 1–3wt% based on acid-base titration (43).

End Functionalization

As the carbon atoms at the ends have larger curvature than carbon atoms in the side-wall, they can be oxidized more easily than other carbon atoms. The end (and defect) functionalization of the CNTs has important ramifications:

1. End functionalization does not destroy the extended π - network, thereby retaining the unaltered electronic and mechanical properties of the CNTs.
2. End functionalization can dramatically change the chemical and physical properties of CNTs, enhance their solubility and facilitate the manipulation of CNTs (44–46) (Figure 4).

The functionalization methodology was based on the amidation of SWCNTs with a long-chain amine [octadecylamine (ODA)]. Acid-treated SWCNTs were first reacted with thionyl chloride to form an acyl chloride intermediate (26). Then the acyl chloride intermediate was heated with ODA at 90–100°C for 96 hours. The resulting amide form of SWCNTs was soluble in many common organic solvents, including chloroform, dichloromethane, aromatic solvents (e.g., benzene, toluene, chlorobenzene) and CS_2 . The solubility of the *s*-SWCNTs in 1,2-dichlorobenzene and CS_2 is higher than 1 mg/mL. This important finding not only provides a new method for obtaining well-characterized highly purified SWCNT materials by separating soluble SWCNTs from insoluble impurities (46,47) but also opens the door for the study of SWCNT chemistry in the organic solution phase. Various solution spectroscopies can be applied to characterize the dissolved SWCNTs (27,47,48).

Based on the same method, other amines such as 4- dodecyl-aniline (48); glucosamine (50); and amine-rich polymers, dendra and proteins (50–52) have been used to functionalize SWCNTs. The methodology of these reactions is based on amidation via acyl chloride intermediate or the 1-ethyl-3(3-dimethylaminopropyl) carbodiimide (EDAC)- or 1,3-dicyclohexylcarbodiimide (DCC)-activated reaction. The poly(propionylethylenimine-co-ethylenimine (PPEI-EI) (53) and bovine serum albumin (BSA)-functionalized SWCNTs (54) are quite soluble in water as well as organic solvents. Sonication during the reaction can promote EDAC-activated amidation (53). The ring closure of SWCNTs by reaction between the $-\text{COOH}$ and $-\text{OH}$ at their ends has also been reported (55).

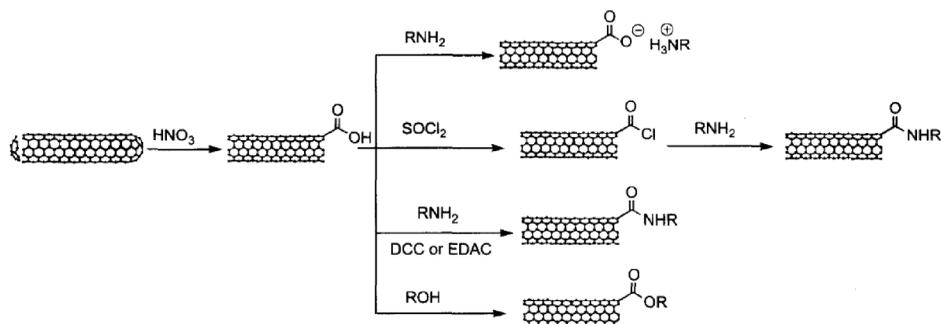


Figure 4. Schematic representation of end functionalization of SWCNTs.

Sidewall Functionalization

As the carbon bonds in the sidewall of the CNTs are of lower reactivity than the bonds in fullerenes, reagents with high chemical reactivity have been involved in the sidewall functionalization of CNTs. Such reagents include carbene (25,27,29), fluorine (28), aryl radical (33,34,55) and azomethine ylides (32). Several methods for the metal reduction of SWCNTs have also been reported (25,31), and SWCNTs with alkyl substituent's were obtained by treating the fluorinated SWCNTs with nucleophilic reagents such as alkyllithium and alkyl magnesium bromides (56–59). Once the sidewall functionalization of SWCNTs had been accomplished, the properties of the SWCNTs change dramatically. The carbon atoms on the sidewalls of SWCNTs that react with functional groups are converted from sp^2 into sp^3 hybridization. The saturation of the π -network leads to a significant change in the electronic band structure of SWCNTs that can be monitored by optical spectroscopy (27,29,30). The presence of sp^3 -hybridized carbon atoms in the SWCNT framework can be detected by Raman spectroscopy (28,30,33,57) and is reflected by an increase in the relative intensity of the disorder mode of the SWCNTs after sidewall functionalization. The solubility of sidewall-functionalized SWCNTs in organic solvents or water is usually improved by the addition of different functional groups.

Noncovalent Functionalization

The advantage of noncovalent functionalization is that it does not destroy the conjugation in the CNTs. One strategy for noncovalent functionalization is based on the usage of an amphiphilic molecule or polymer to interact with CNTs via its hydrophobic pm, whereas the hydrophilic part of this molecule can enhance the solubility of CNTs or react with other molecules. Another method is the ionic interaction of SWCNTs, which leads to the formation of acid-base salts or charge-transfer complexes. For example, the acid form of SWCNTs was heated with melted octadecylamine to form an SWCNT carboxylate zwitterion (60). Such a form of SWCNTs is soluble (>0.5 mg/mL) in tetrahydrofuran and 1,2-dichlorobenzene. Generally, a 0.1 mg/mL solution is stable for more than 10 days and is visually nonscattering. The majority of the SWCNT ropes were exfoliated into small ropes (2–5 nm in diameter) and individual SWCNTs with length of several micrometers during the dissolution process. Noncovalent functionalization of SWCNTs has been achieved by using small molecules such as 1-pyrenebutanoic acid succinimidyl ester (60). This amphiphilic molecule can attach to the surface of SWCNTs by π - π interaction with the pyrene moiety, while the hydrophilic ester of this molecule enhances the solubility of SWCNTs. This approach has been used in protein immobilization, including the study of ferritin, streptavidin and biotin-PEO-amine. These bioactive molecules have been attached to the surface of SWCNTs via a nucleophilic substitution of N-hydroxysuccinimide by using the amine group on the proteins to form an amide. Molecules of high molecular weight can wrap themselves around the surfaces of SWCNTs. Polymers, including polyvinyl pyrrolidone (PVP) and polystyrene sulfonate (PSS), poly (phenylacetylene) (PPA) (61), poly(metaphenylenevinylene) (PmPV) (62), poly[arjleneethynylenes (PPE) (63), poly-anisidine (POAS) (64), amylose (65), amphiphilic copolymer poly(styrene)-block-poly (acrylic acid) (66) and natural polymer (65), have been used to wrap or encapsulate CNTs. The interaction between the CNTs and the polymer hosts usually originates from the van der Waals interaction between the surface of the CNTs and the hydrophobic part of the host polymer. The mechanism of these polymer-wrapping methods depends on both the interaction between SWCNTs and

polymers, and the structure of the polymers. A thermodynamically driven model for wrapping SWCNTs has been suggested, wherein the polymer disrupted both the hydrophobic interface with water and nanotube-nanotube interactions in the CNT (66) aggregates. AFM investigation revealed that the individual PVP-SWCNT displayed a uniform diameter along its length, which indicates that the polymers were uniformly wrapped along the surface of the SWCNTs rather than being randomly attached. A helical wrapping model was used to explain the solubilization of SWCNTs at the molecular level. In another case, a straight, rigid polymer, poly (aryleneethynylene) (PPE), has been used to interact with SWCNT (63–67). Because the polymer is short and rigid, it attached to the surface of SWCNTs in a non wrapping form parallel to the nanotube axis (Figures 5–6).

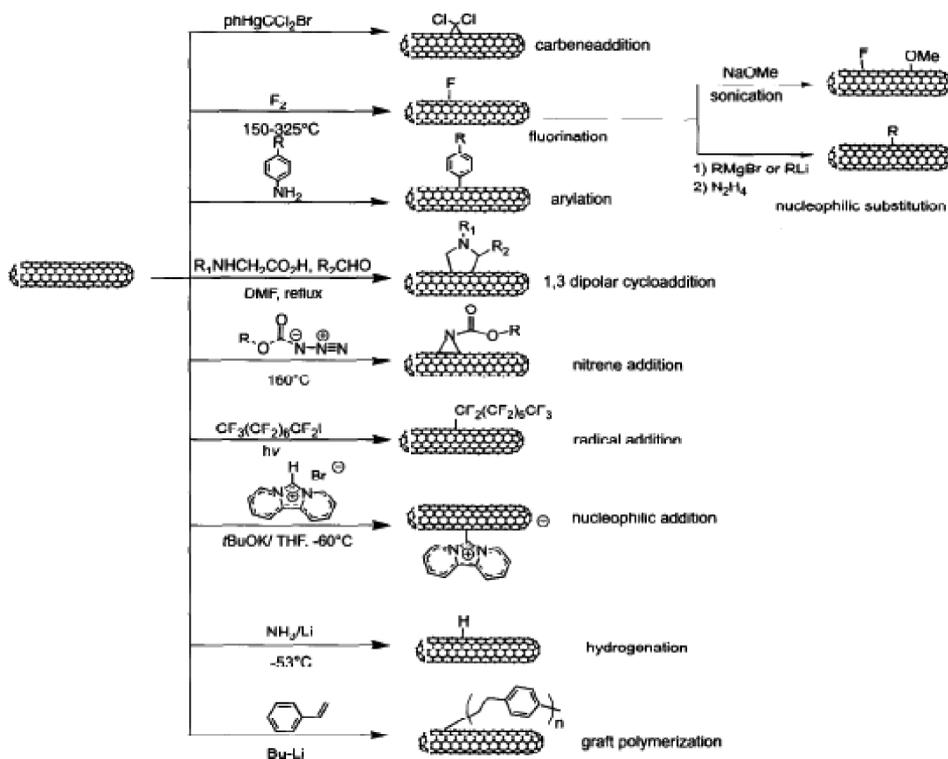


Figure 5. Schematic representation of sidewall functionalization of SWCNTs.

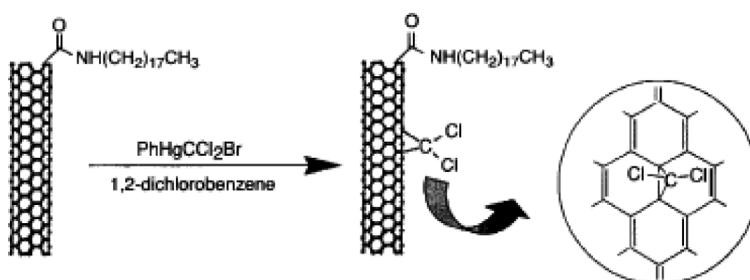


Figure 6. Schematic representation of dichlorocarbene addition to soluble SWCNTs.

Application of Chemistry Functionalized Carbon Nanotubes

The functionalized CNTs can have higher solubility or differing molecular affinity or electronic response, and this allows for more effective use of their outstanding electronic and mechanical properties. It is clear that CNTs will find applications in electronics, sensors, composite materials, biology and medicine. The strength and high aspect ratio of CNTs are particularly valuable in the design of probe tips for scanning probe microscopy (68–71), electrochemistry (71) and biological analysis (72,73). Using carbodiimide chemistry, carboxyl groups at the tip ends coupled with different amines to form amide-linked groups. By employing the characteristic properties of these amide groups, this chemically modified MWCNT probe could be used for titrating acid and base groups, to image patterned samples based on molecular interactions and to measure the binding force between single protein-ligand pairs. Individual semiconducting SWCNT-based chemical sensors are reliable for the detection of small amounts of gases such as NH_3 and NO_2 (74). The mechanism of this sensor action is based on charge transfer between the SWCNTs and NO_2 or NH_3 . Exposure to the gases affected the electronic properties of the SWCNTs and led to a change in the conductivity. It was observed that the conductance of the SWCNT sample dramatically increased in NO_2 and decreased in NH_3 .

Recently, there has been intense interest in exploring the novel properties of CNTs, especially SWCNTs for biological applications. The 1-D structure of SWCNTs makes them an ideal candidate for the development of a new generation of biodevices. Because SWCNTs are molecular wires with every carbon atom exposed on the surface, SWCNTs are promising candidates for the development of extremely sensitive biosensors. Because of their small dimensions, SWCNTs can be easily introduced into cells with little or no disturbance of the cell function. In addition, the outstanding electronic properties of SWCNTs will allow biological events to be addressed electronically. The progress in understanding the interactions between CNTs and biomolecules has stimulated extensive research on the fabrication of bionanodevices and especially biosensors. SWCNT devices have shown high sensitivity in the detection of redox enzyme (75–77), DNA (78) and proteins (79).

An alternative approach to tethering biological molecules to SWCNTs in a controlled manner is covalent functionalization. Covalent functionalization provides better integrity, stability and reproducibility of the fabricated devices. Typically, covalent binding of proteins and enzymes utilizes the diimide-activated amidation of carboxylic acid-functionalized carbon nanotubes as schematically illustrated in Figure 7 (paths a and b) (54,80–82). For covalent attachment of DNA, amine-terminated SWCNTs are cross-linked with succinimidyl 4-(N-maleimidomethyl) cyclohexane-1-carboxylate (SMCC) to produce maleimide groups further reacted with thiol-terminated DNA (path c) (83) (Figure 7). A method for functionalization of SWCNTs with N-protected amino acids based on the 1, 3-dipolar cyclo addition reaction to the external walls of SWCNTs has also been reported (84–105) (Figure 8).

Conclusion

The chemistry of CNTs has made enormous strides, and it is clear that this subject will drive the applications of carbon nanotubes. In order to further refine the chemically functionalized CNTs, it is important to begin the chemistry with high quality materials. Functionalization of individual CNT, and particularly CNTs of defined length, diameter and chirality, is the next step that will lead to the control of CNT-based materials and devices at the molecular level.

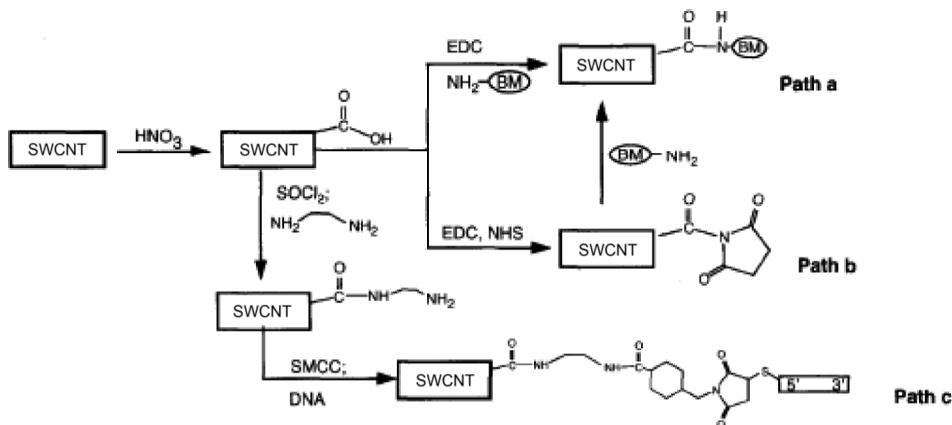


Figure 7. Schematic representation of functionalized SWCNTs in biological application.

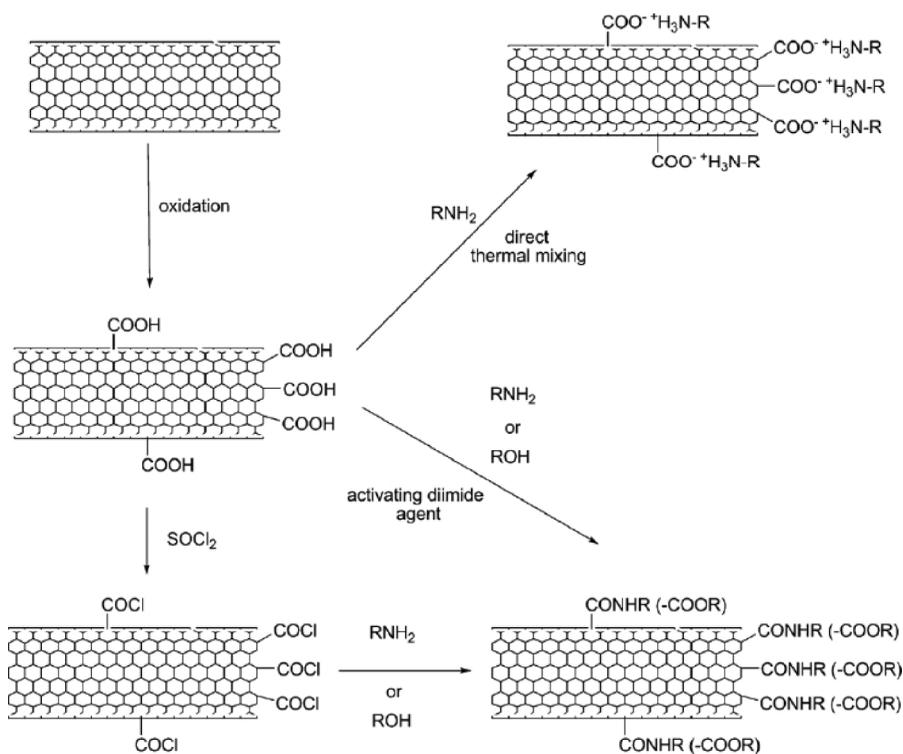


Figure 8. Oxidation of CNTs and derivatization reaction with amines or alcohols.

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