Chemically Functionalized Carbon Nanotubes

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From the Contents

Graffiti art of the letters N A N O
Spraypaint on canvas, 170 cm × 130 cm,
by LOOMIT, Munich 1999
Courtesy: Prof. Alf Mews, University of Siegen
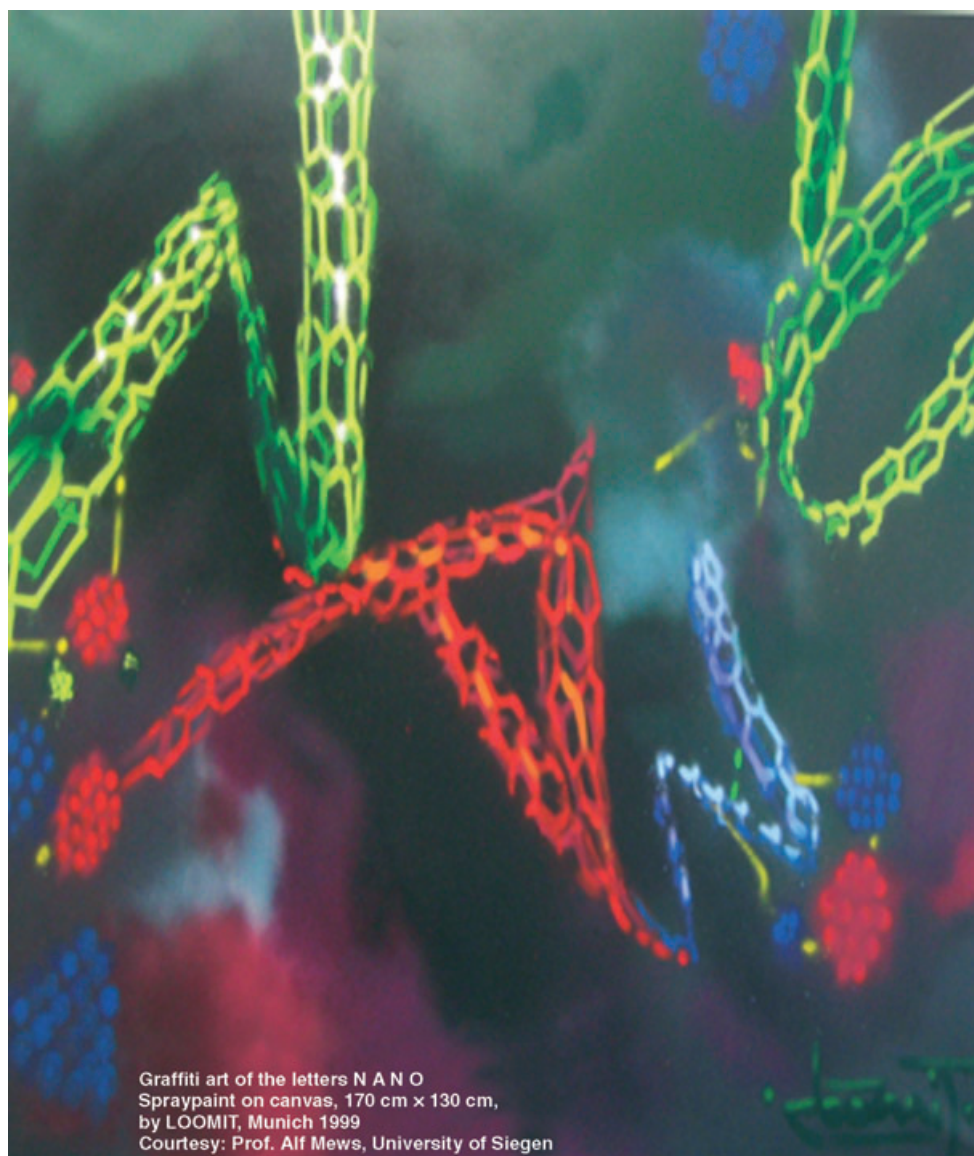
Artist's view of carbon nanotubes functionalized with fluorescing particles.

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Keywords:
- carbon nanotubes
- chemical functionalization
- electrochemical modification
- photochemistry
- sensors

*S*ince their discovery, carbon nanotubes have attracted the attention of many a scientist around the world. This extraordinary interest stems from their outstanding structural, mechanical, and electronic properties. In fact, apart from being the best and most easily available one-dimensional (1D) model system, carbon nanotubes show strong application potential in electronics, scanning probe microscopy, chemical and biological sensing, reinforced composite materials, and in many more areas. While some of the proposed applications remain still a far-off dream, others are close to technical realization. Recent advances in the development of reliable methods for the chemical functionalization of the nanotubes provide an additional impetus towards extending the scope of their application spectrum. In particular, covalent modification schemes allow persistent alteration of the electronic properties of the tubes, as well as to chemically tailor their surface properties, whereby new functions can be implemented that cannot otherwise be acquired by pristine nanotubes.

1. Introduction

Carbon nanotubes (CNTs) are cylinder-shaped macromolecules with a radius as small as a few nanometers, which can be grown up to 20 cm in length.[1] The walls of these tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. They are capped at their ends by one half of a fullerene-like molecule. In the most general case, a CNT is composed of a concentric arrangement of many cylinders (Figure 1). Such multi-walled nanotubes (MWCNTs) can reach diameters of up to 100 nm. A special case of these multi-walled tubes is the double-walled CNT composed of just two concentric cylinders. Single-walled nanotubes (SWCNTs) possess the simplest geometry, and have been observed with diameters ranging from 0.4 to 3 nm. The formation of a SWCNT can be visualized through the rolling of a graphene sheet. Based on the orientation of the tube axis with respect to the hexagonal lattice, the structure of a nanotube can be completely specified through its chiral vector (see Figure 2), which is denoted by the chiral indices (n, m). The classification of the nanotubes as armchair $(n = m)$ or zigzag $(m = 0)$ has its origin from the geometric arrangement of the carbon atoms at the seam of the cylinders. While both these types of tubes possess mirror symmetry, nanotubes with $m \neq n$ are chiral. The latter kind of tubes exists as two enantiomers with right- and left-handed helicity. Historically the multi-walled nanotubes were the first to be discovered (1991),[2] followed by their single-walled counterparts (1993).[3] In the meantime, CNTs have emerged to be one of the most intensively investigated nanostructured materials.[4] This is reflected, for instance, by the continuously increasing number of publications, which exceeded three thousand in the year 2003.

Three different methods are now well established for the production of SWCNTs (see Table 1). Among these, the catalytic decomposition of a gaseous carbon feedstock (e.g., CO[5]) offers the highest production rate (≈ 50 kg day^{-1}).
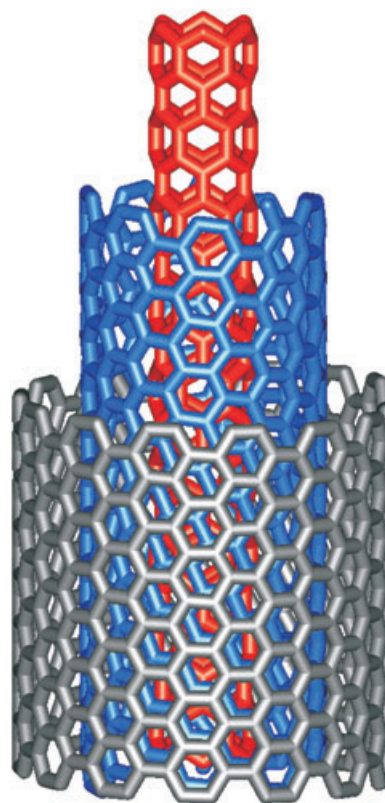

Figure 1. Structure of a multi-walled carbon nanotube made up of three shells of differing chirality.

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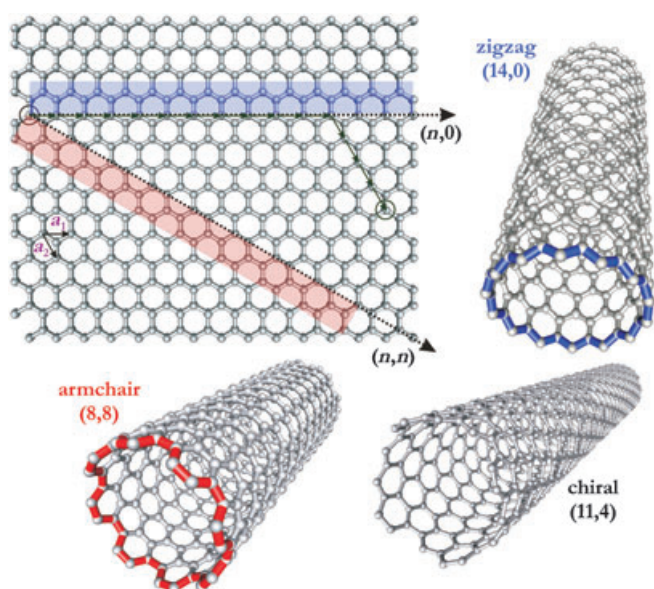Fax: (+49) 711-6891662
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Figure 2. Roll-up of a graphene sheet leading to the three different types of CNT.

However, despite the remarkable progress made in the synthesis methods during the last 3–4 years, the costs are still too high for large-scale applications of the nanotubes. The current price for SWCNTs is around 50–100 Euros per gram,[6] and the purity of such samples is still lagging behind that of standard laboratory reagents. The raw material usually contains amorphous carbon, fullerenes, and catalytic metal particles (e.g., Co or Ni) as impurities. Consequently, an effective purification of the nanotubes is required before their further processing. A typical state-of-the-art purification scheme[7] is illustrated in Scheme 1. In the first step, the amorphous carbon is removed by oxidation upon heating to $\approx 350\,°C$ in air. Following this, the freed metal particles are removed by heating in a non-oxidizing acid solution. Through a final annealing at a temperature in excess of $1000\,°C$ in vacuum, most of the defects created in the earlier steps can be removed.

Procedures for the synthesis of large quantities of nanotubes invariably deliver bundles, which are composed of up to hundreds of single nanotubes. To enable easy access for chemical reagents, however, it is advantageous to have individually dispersed nanotubes instead of bundles. For this purpose, ultrasonic treatment of the CNTs in an aqueous surfactant solution has been shown to be effective,[8] which leads to the enclosure of the individual tubes in a detergent shell. It should be stressed that the experimental conditions have to be carefully controlled, since intensive ultrasonication may cause severe damage to the tube walls.[9]

Alternatively, isolated and relatively pure SWCNTs can be directly synthesized by chemical vapor deposition (CVD) on a solid support, albeit in smaller quantities (Scheme 2). In this approach,

Table 1. Overview of the important synthesis procedures for single-walled carbon nanotubes.

| Synthesis method	Principle	Average diameter of the tubes	Maximum production rate
Electric arc-discharge	Carbon atoms are generated through an electric arc discharge at $T > 3000\,°C$ between two graphite rods. Nanotubes are formed in the presence of suitable catalyst metal particles (Fe, Co, or Ni).	1.3–1.4 nm	120 g day^{-1}
Laser ablation	Generation of atomic carbon at $T > 3000\,°C$ through laser irradiation of graphite, which contains appropriate catalyst particles (Fe, Co, or Ni), is followed by formation of nanotubes.	1.4 nm	50 g day^{-1}
Catalytic decomposition of gaseous hydrocarbons	Decomposition of a gaseous hydrocarbon source (e.g., an alkane or CO) is catalyzed by metal nanoparticles (Co or Fe). Particles are prepared by pyrolysis of suitable precursors (e.g., $[Fe(CO)_5]$) at 1000–$1100\,°C$ under high pressure.	1 nm	50 kg day^{-1}

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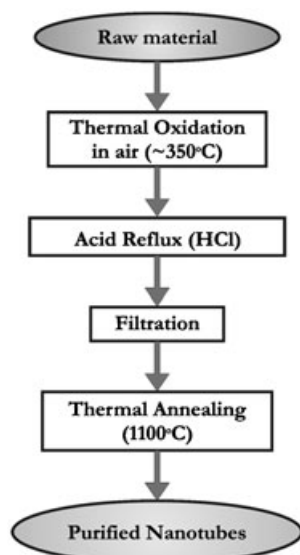
Scheme 1. The purification process for SWCNTs.

catalyst particles are deposited onto a substrate, and individual SWCNTs with uniform diameters are grown at elevated temperatures ($>600\,°C$) from the catalyst particles, using for instance methane[10] or an alcohol vapor[11] as the carbon source. An appealing feature of this method is the possibility to control the diameter of the produced tubes through the size of the catalyst particles.[12] With the help of lithographic techniques, isolated SWCNTs grown in this manner can then directly be contacted by electrodes, and their electrical properties investigated in detail.[13]

Since the emergence of carbon nanotubes, their electrical properties have attracted particular interest. According to the zone-folding approach, which derives the electronic structure of nanotubes directly from graphite, a nanotube behaves either as a metal or as a semiconductor, depending on its chiral vector.[14] Within a sample showing no preference for specific chiralities, one third of the tubes are expected to be metallic, and the remaining two thirds to be semiconducting. Furthermore, the bandgap in semiconducting tubes is predicted to scale inversely with their diameter. Both of these predictions have been verified through numerous experimental results.[15] Marked deviations from the zone-folding scheme are encountered only for SWCNTs that have the smallest diameters (≤ 0.5 nm).[16]

Upon cooling, the electrical resistance of a metallic nanotube decreases, which can be attributed to the reduced scattering of electrons by lattice vibrations.[17] Semiconducting nanotubes, on the other hand, exhibit an opposite be-

havior, that is, with decreasing temperature their resistance increases due to a reduced number of carriers that are able to overcome the bandgap.[18] The electrical conductivity of semiconducting tubes can be effectively modulated by an external electric field, which makes them suitable for use as high-performance field-effect transistors.[19] As-prepared semiconducting nanotubes that are not subjected to specific treatments principally exhibit p-type semiconducting characteristics, where holes are the majority carriers. By comparison, the conductivity of metallic nanotubes is barely influenced by the application of a gate voltage, unless the tubes contain an appreciable amount of defects.[20] Electrical measurements are thus routinely used to distinguish between a metallic and a semiconducting nanotube (Figure 3).
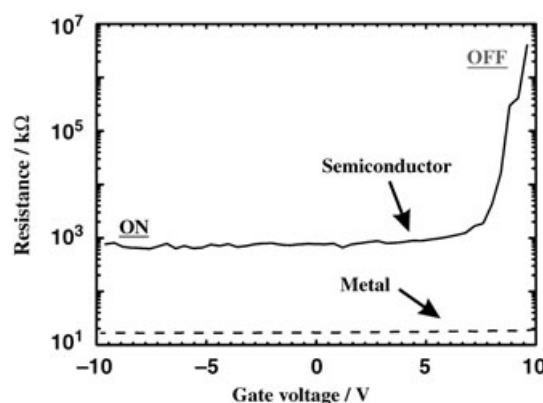

Figure 3. Dependence of the room-temperature resistance of a metallic and a semiconducting SWCNT on an external gate voltage.

On top of their excellent electrical properties, carbon nanotubes possess high mechanical and chemical stability. While the latter is certainly advantageous from an application point of view, this attribute also imposes a severe hurdle for the development of methods allowing for the selective and controlled covalent functionalization of the nanotubes. This explains why it was only within the past 3–4 years that a wider range of reliable functionalization schemes have become available. In this Review, relevant methods for the covalent functionalization of SWCNTs will be presented, together with some of the resulting applications. Although covalent functionalization methods have also been developed for MWCNTs,[21] fewer investigations have been devoted to this type of nanotubes. Covalent functionalization of SWCNTs has been accomplished by three different approaches, namely, thermally activated chemistry,
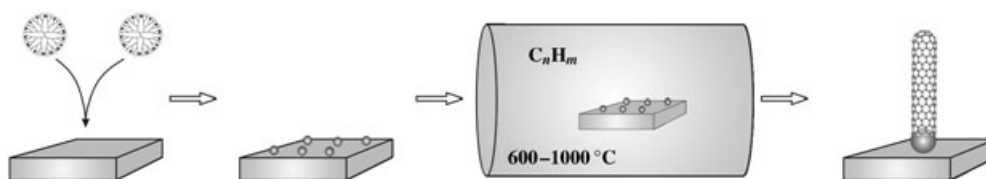
Scheme 2. Synthesis of individual CNTs by CVD using clusters of catalyst particles deposited on a substrate.

electrochemical modification, and photochemical functionalization.

Ideal SWCNTs possess two distinct regions of differing reactivity towards covalent chemical modification. The presence of five-membered rings at the caps leads to a relatively higher reactivity at these points, comparable to the reactivity of fullerenes.[22] By comparison, functionalization of the sidewall comprising the regular graphene framework is more difficult to accomplish. In general, addition reactions to the partial carbon–carbon double bonds cause the transformation of sp^2- into sp^3-hybridized carbon atoms, which is associated with a change from a trigonal-planar local bonding geometry to a tetrahedral geometry. This process is energetically more favorable at the caps due to their pronounced curvature in two dimensions, in marked contrast to the sidewall with its comparatively low curvature in only one dimension. On the other hand, the non-zero curvature makes the sidewall more reactive than a planar graphene sheet. Correspondingly, the binding energy of atoms or functional groups on the sidewall should increase with decreasing tube diameter. This tendency is supported by theoretical studies, as has been reported, for instance, for the bonding of alkyl radicals to the sidewall of a SWCNT.[23] On the contrary, the concave curvature of the inner surface of the nanotube imparts a very low reactivity towards addition reactions,[24] so that carbon nanotubes have been proposed as nano-containers for reactive gas atoms, analogous to fullerenes encapsulating nitrogen atoms (e.g., N@C$_{60}$).

In reality, however, nanotubes are not ideal structures, but rather contain defects formed during synthesis. Typically around 1–3% of the carbon atoms of a nanotube are located at a defect site.[25] A frequently encountered type of defect is the so-called Stone–Wales defect, which is comprised of two pairs of five-membered and seven-membered rings, and is hence referred to as a 7-5-5-7 defect (Figure 4). A Stone–Wales defect leads to a local deformation of the
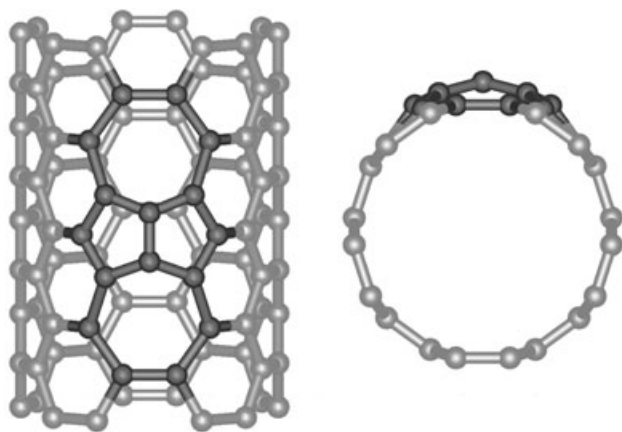
of this curvature, addition reactions are most favored at the carbon–carbon double bonds in these positions.[26]

2. Thermally Activated Chemical Functionalization

2.1. CNT Oxidation and Carboxyl-Based Couplings

A major milestone in the emerging area of nanotube chemistry was the development of an oxidation process for SWCNTs involving extensive ultrasonic treatment in a mixture of concentrated nitric and sulfuric acid.[27] Such drastic conditions lead to the opening of the tube caps as well as the formation of holes in the sidewalls, followed by an oxidative etching along the walls with the concomitant release of carbon dioxide. The final products are nanotube fragments with lengths in the range of 100 to 300 nm, whose ends and sidewalls are decorated with a high density of various oxygen containing groups (mainly carboxyl groups). Under less vigorous conditions, such as refluxing in nitric acid, the shortening of the tubes can be minimized. The chemical modification is then limited mostly to the opening of the tube caps and the formation of functional groups at defect sites along the sidewalls. Nanotubes functionalized in this manner basically retain their pristine electronic and mechanical properties.[28]

The oxidatively introduced carboxyl groups represent useful sites for further modifications, as they enable the covalent coupling of molecules through the creation of amide and ester bonds (Figure 5). By this method the nanotubes can be provided with a wide range of functional moieties,

Figure 4. Stone–Wales (or 7-5-5-7) defect on the sidewall of a nanotube.

graphitic sidewall and thereby introduces an increased curvature in this region. The strongest curvature exists at the interface between the two five-membered rings; as a result
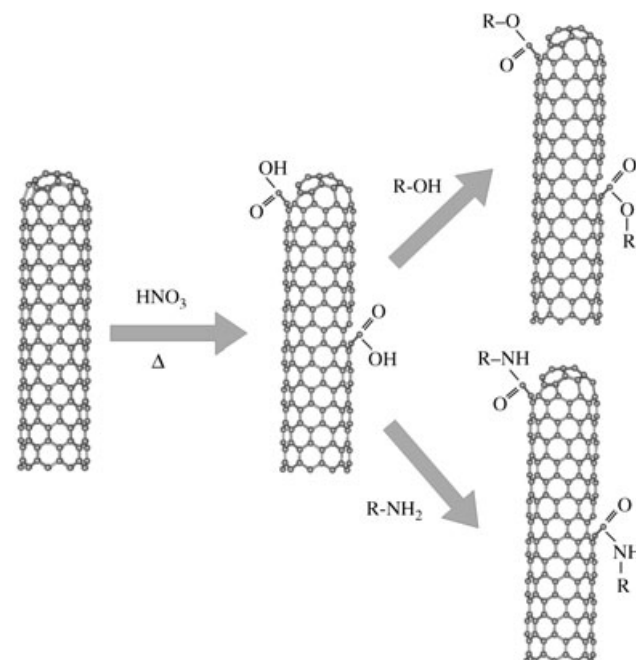

Figure 5. Chemical modification of nanotubes through thermal oxidation, followed by subsequent esterification or amidization of the carboxyl groups.

for which purpose bifunctional molecules (e.g., diamines) are often utilized as linkers. Illustrative examples are nanotubes equipped with dendrimers, nucleic acids, enzymes, metal complexes, or semiconductor and metal nanoparticles.[29] Another interesting application of the carboxyl groups is the formation of an anhydride at the tube ends, through which rings of nanotubes are accessible.[30]

The presence of (modified) carboxyl groups leads to a reduction of van der Waals interactions between the CNTs, which strongly facilitates the separation of nanotube bundles into individual tubes. Additionally, the attachment of suitable groups renders the tubes soluble in aqueous or organic solvents, opening the possibility of further modifications through subsequent solution-based chemistry. A high water solubility of a few tenths of a gram per milliliter has recently been achieved on the basis of the carboxyl-based coupling of hydrophilic polymers such as poly(ethylene glycol) (PEG).[31] SWCNTs with a good solubility in organic solvents can be obtained by covalent[32] or ionic[33] attachment of long-chain aliphatic amines onto the carboxyl groups.

2.2. Addition Reactions at the Sidewall

While the two-step functionalization of nanotubes through the oxidative introduction of carboxyl groups followed by the formation of amide or ester linkages does allow for a stable chemical modification, it has only a relatively weak influence on the electrical and mechanical properties of the nanotubes. By comparison, addition reactions enable the direct coupling of functional groups onto the π-conjugated carbon framework of the tubes. The required reactive species (atoms, radicals, carbenes, or nitrenes) are in general made available through thermally activated reactions, and small-diameter tubes are preferred as they show higher chemical reactivity due to their increased curvature.[34] A series of addition reactions have been well documented, the most important of which are listed in Figure 6.
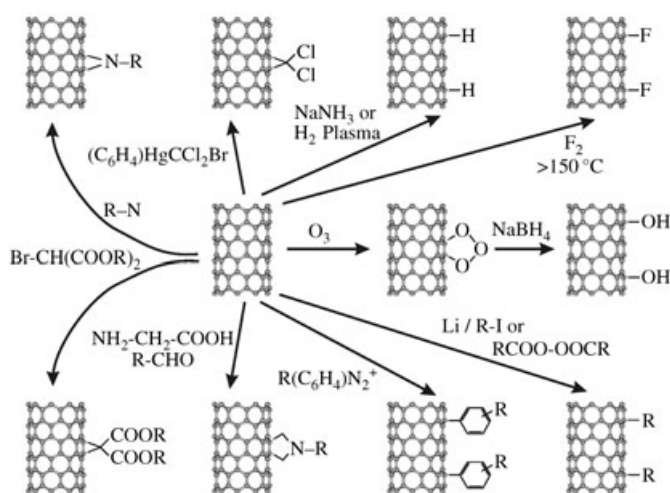
While in the initial experiments aiming at addition reactions to the sidewall only one to three functional groups were found per 100 carbon atoms,[35] the procedures developed more recently have reached functionalization degrees of at least 10%.[36] At the present stage, however, the addition mechanisms are not yet completely understood. In principle, the addition reaction could be initiated exclusively on the intact sidewall, or in parallel at defect sites from where the reaction could proceed further. For most of the reactions shown in Figure 8, it is a matter of actual investigation as to which extent these two possibilities contribute. One exception is nanotube fluorination, for which direct addition to the defect-free sidewall appears viable.[37] Nonetheless, the addition of fluorine has a noticeable activation barrier, due to which the reaction requires slightly elevated temperatures ($T > 150\,°C$).

Analogous to nanotube functionalization with carboxyl groups, the direct covalent attachment of functional moieties to the sidewalls strongly enhances the solubility of the nanotubes. The good solubility of nanotubes modified with organic groups has been exploited for their effective purification.[38] In this procedure, small particles are first separated from the solution through chromatography or filtration, and then the covalently attached groups are removed through thermal annealing ($T > 250\,°C$).

2.3. Substitution Reactions on Fluorinated Nanotubes

The fluorine atoms in fluorinated carbon nanotubes can be replaced through nucleophilic substitution reactions with relative ease, thus opening a flexible approach for providing the sidewalls with various types of functional groups, as illustrated in Figure 7. As nucleophilic reagents, alcohols,
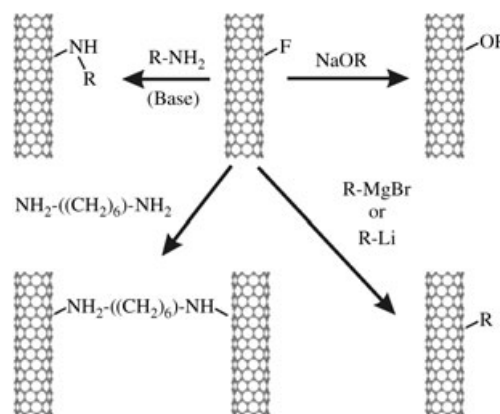
Figure 7. Functionalization of the sidewall through nucleophilic substitution reactions in fluorinated nanotubes.

amines, Grignard reagents, and alkyl lithium compounds have been successfully employed, which have resulted in up to 15% of the carbon atoms of the sidewall bearing a functional group.[39] Moreover, by using a bifunctional reagent, such as an α,ω-diamine with a sufficiently long carbon chain, the nanotubes can be covalently cross-linked with each other.[40]

Figure 6. Overview of possible addition reactions for the functionalization of the nanotube sidewall.

3. Electrochemical Modification of Nanotubes

Interest in the study of the electrochemical properties of CNTs mainly stems from their superior electrocatalytic properties and their high surface-to-volume ratio, as compared to other carbon materials that are widely used as electrode materials.[41] As a result of this interest, electrochemistry has been developed into an elegant tool for the functionalization of CNTs in a selective and controlled manner. To this end, a constant potential (potentiostatic) or a constant current (galvanostatic) is applied to a CNT electrode immersed in a solution that contains a suitable reagent, whereby a highly reactive (radical) species is generated through electron transfer between the CNT and the reagent. Many organic radical species have a tendency to react with the starting reagent or to self-polymerize, resulting in a polymer coating on the tubes. Depending on the reagent used, the polymeric layer may or may not be bonded in a covalent manner on to the nanotube sidewall. In addition to being simple, clean, and efficient, electrochemical modification (ECM) schemes are quite versatile in that they allow for an accurate control over the extent of film deposition through the choice of suitable electrochemical conditions, that is, the duration and magnitude of the applied potential. Moreover, by utilizing reagents containing appropriate substituents, the surface properties of the coated tubes can be tailored, for example, from highly polar to predominantly hydrophobic. ECM has proven to be a suitable tool to modify entangled SWCNTs networks as well as individual SWCNTs.

3.1. Covalent ECM of CNTs in Bulk

Via electrochemical coupling of aromatic diazonium salts, phenyl residues have been covalently grafted onto bulk samples of SWCNTs.[42] In one of the first experiments performed in this direction, phenyl rings bearing various substituents were covalently linked to a SWCNT paper. The Raman spectra of the SWCNT paper exhibited noticeable changes after modification, most importantly an increase in the relative intensity of the D-line at ≈ 1290 cm^{-1}, which is known to be sensitive to disorder within the sp^2-bonded carbon framework.[43] In addition, a significant decrease in the intensity of the radial breathing mode (RBM) has been detected, which indicates a strong disturbance in the hexag-

onal lattice of the sidewalls. The extent of modification has been found to vary depending on the type of aryl diazonium salt used. After ECM, up to one in 20 carbon atoms has been found to possess an aromatic residue corresponding to a functionalization degree of 5%. The coupling mechanism has been interpreted to involve the transfer of an electron from the CNT, which reduces the diazonium salt to a highly reactive phenyl radical that then attaches covalently to the sidewall. More recently, the formation of aryl chains on the sidewalls of the nanotubes has been proven from Raman spectroscopic studies.[44] Although the first electrochemical couplings were achieved with HIPCO-produced SWCNTs, whose reactivity is enhanced by their small diameters of down to 0.6 nm,[45] large-diameter nanotubes are also found to be amenable to covalent ECM under specific conditions.[46]

3.2. ECM of Single Nanotubes

The high capability of ECM becomes especially apparent when applied to individual nanotubes, as has been demonstrated by the covalent attachment of substituted phenyl groups to electrically addressable individual SWCNTs via the diazonium coupling route.[47] This method yields homogeneous tube coatings with a thickness as low as 3–4 nm (Figure 8). The layer thickness is found to increase with the duration of ECM, the magnitude of the applied potential, and the concentration of the diazonium salt, together providing access to coatings with a thickness of up to 15 nm. Detailed investigations on the effect of grafted coatings on the electronic and structural properties still remain a challenging task when they have to be performed at the single-nanotube level. For this aim, a combination of electrical transport measurements and confocal Raman microscopy has proven to be especially useful.[46] The diazonium coupling causes an increase in both the electrical resistance and the relative Raman D-line intensity, as demonstrated in Figure 9 for a metallic SWCNT. Combined electrical and Raman studies furthermore allow differentiation between changes in semiconducting tubes that arise from doping from those due to covalent modification of their carbon framework. This is illustrated by Figure 10 for a semiconducting SWCNT modified by electrodeposition of a thin polymer layer (≈ 4 nm thickness) of a substituted aromatic
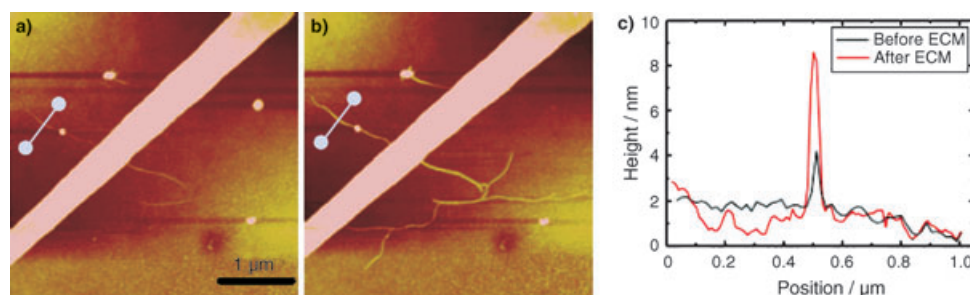

Figure 8. Electrochemical modification (ECM) of an individual electrically contacted SWCNT using a diazonium salt: Atomic force microscope (AFM) images before (a) and after (b) modification; c) line profiles along the lines marked in the AFM images before and after ECM.
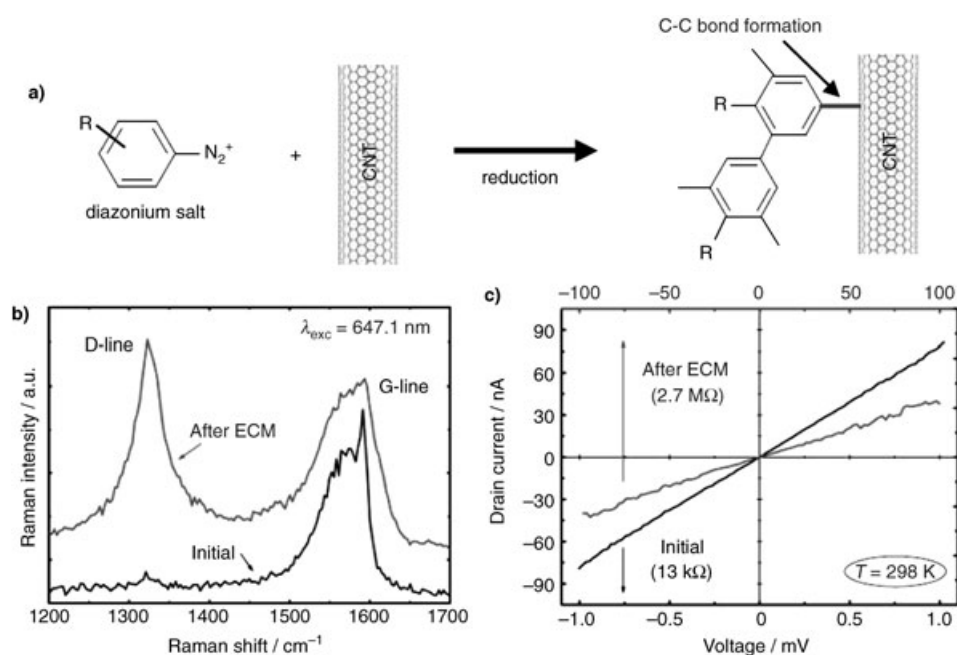
Figure 9. a) Reaction scheme for reductive ECM with an aromatic diazonium salt; b) Raman spectra and c) I–V curves of an individual metallic SWCNT before and after ECM.
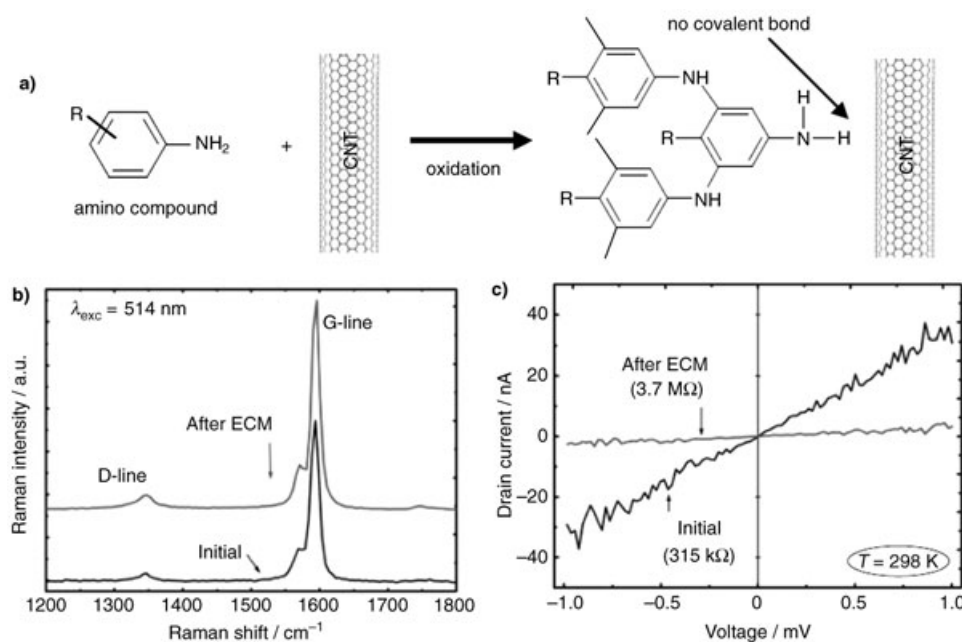
Figure 10. a) Reaction scheme for oxidative ECM with a substituted aromatic amine; b) Raman spectra and c) I–V curves of an individual semiconducting SWCNT before and after ECM.

4. Photochemical Functionalization of Nanotubes

In contrast to the chemical functionalization routes based upon thermally activated chemistry or electrochemistry, photochemical approaches have been employed to a much lesser extent up to now. Photoirradiation has been used to generate reactive species such as nitrenes in the course of sidewall addition reactions.[48] In these cases however, the photoactivation exclusively employs the azido compound as the nitrene precursor. Only one case of "true" photochemical modification of SWCNTs has been reported to date, which is sidewall osmylation.[49,50] Initially, it was observed that SWCNTs exposed to osmium tetroxide (OsO_4) under UV-light irradiation show a pronounced increase in electrical resistance (Figure 11). This change has been ascribed to the photoinduced cycloaddition of OsO_4 to the partial carbon–carbon double bonds, as a result of which the π-electron density in the nanotubes is decreased. It is interesting to note that when humidity is carefully avoided, the OsO_4 addition is reversible, that is, the cycloadduct can be cleaved by photoirradiation, whereby the original resistance is restored. In a later study, UV-light-induced osmylation of SWCNTs was also studied in organic solvents.[50] Under these conditions, OsO_4 appears to react preferentially with the metallic tubes contained within the

amine. While the tube clearly displays a resistance increase after the coating, the D-band in the Raman spectrum is almost unaffected. These observations indicate that the created radical cations do not covalently attach to the nanotube wall, which leaves the observed increase in resistance to be attributed to n-type doping upon oxidation of the amine, thus leading to a reduced hole concentration in the p-type tubes.

sample. This selectivity may originate from the availability of electronic states at the Fermi level in the metallic tubes, which facilitates the formation of an intermediate charge-transfer complex. As distinguished from the reactions performed by exposure to gaseous OsO_4, the major product in the organic medium are SWCNTs decorated with OsO_2 particles, resulting in the formation of extended tube aggregates. This difference most likely arises from the fact that in
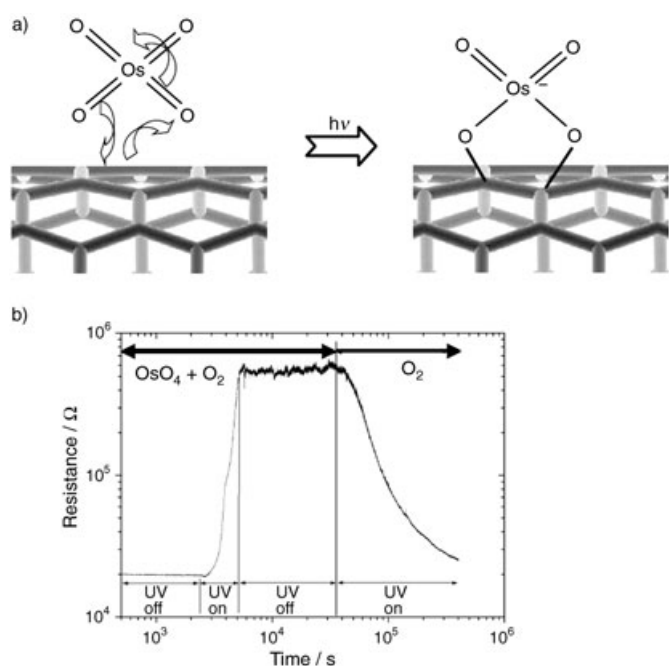
Figure 11. a) Reaction scheme for sidewall osmylation of a SWCNT using UV light; b) resistance change of an individual metallic SWCNT upon exposure to OsO_4 and O_2 under UV-light irradiation.

the latter case, the cycloadduct is readily hydrolyzed by the presence of traces of water.

5. Applications

The recently developed chemical methods for chemical functionalization of carbon nanotubes have opened up a broad range of novel application perspectives (Table 2). In this Section, five specific applications of (electro-) chemically modified SWCNTs are described in detail.

5.1. Field-Effect Transistors

For many electronic applications it is of great importance to have nanotube ensembles that exhibit uniform electrical properties. While metallic nanotubes are desirable for nanoscale electrical interconnects, the fabrication of transistor devices requires exclusively semiconducting nanotubes. At present there exists no synthesis method that allows for a reliable control over the electrical properties of the produced nanotubes. The raw nanotube material thus constitutes a mixture of metallic and semiconducting nanotubes. Various methods for the separation of the two types of nanotubes have been devised. One such procedure is based upon alternating current dielectrophoresis of surfactant-stabilized SWCNTs,[51] which takes advantage of the differing concentrations of freely movable charge carriers in nanotubes: Metallic nanotubes possess a high density of such carriers, which gives them a large electronic polarizability. Hence, when a suitable alternating electric field is applied, they are attracted to the regions of highest field strength, whereas the semiconducting tubes are repelled. An important disadvantage of this method is that it is limited to very small material quantities. On the other hand, chemical separation methods exploiting differences in the solubility of the two types of tubes upon doping with an electron acceptor offer an easier scalability.[52] However, all currently available chemical methods are still far from enabling an exclusive enrichment of one type of tube.

An alternative technique for the separation of the tubes is based on the selective destruction/functionalization of the metallic nanotubes in a tube ensemble. As one possibility, this can be achieved by applying an increasing electrical voltage across the tube ensemble until the metallic tubes are burnt off as a consequence of Joule heating arising from the high current densities.[53] The procedure is performed by simultaneous application of a gate voltage to deplete the semiconducting nanotubes of charge carriers, so that exclusively the metallic nanotubes remain conductive. While this method has proven effective for the separation of single tubes, its application to samples composed mainly of bundles faces limitations. This is due to the close proximity of the metallic and semiconducting nanotubes within the bundles, which leads to a high risk of damage for the latter type of tubes. Electrochemical methods offer an elegant solution to this problem. Upon switching off the semiconducting tubes under appropriate gate control, the metallic tubes are exclusively provided with a high density of covalently coupled phenyl radicals reductively generated from aromatic diazonium salts (see Sections 3.1 and 3.2). As a

Table 2. Potential applications of chemically modified carbon nanotubes.

(Potential) Application	Function of the covalently bonded moiety
Nanostructured electronic devices, e.g., nanodiodes	Local modification of the electronic band structure
(Bio-) chemical sensors	Selective recognition of analyte molecules
Catalyst supports	Anchoring of molecules or metal nanoparticles
Mechanically reinforced composites	Chemical coupling with a matrix
Chemically sensitive tips for scanning probe microscopy	Selective chemical interaction with surfaces
Field emission	Reduction of the work function for electrons at the tube ends
Nanofiltration	Control of the passage of molecules or ions through steric effects or Coulombic interactions
Artificial muscles	Mechanical stabilization of nanotube films through covalent cross-linking
Controlled drug release	Biocompatibility; recognition of biological fingerprints
Pharmacology	Enzyme inhibition or blocking of ionic channels in the cell membrane
Directed cell growth on surfaces	Specific interactions with cell surfaces

consequence, the modified metallic tubes become insulating, and the resulting ensemble shows purely semiconducting behavior (Figure 12). The conductance of such devices can be varied over many orders of magnitude through the voltage at the gate electrode.[54] The key concept of this approach is the creation of highly reactive radicals exclusively at the locations where the reaction is desired, that is, at the interface between the electrolyte and the metallic nanotubes.

5.2. Chemical Sensors

The fact that all of the carbon atoms in a carbon nanotube are surface atoms makes them optimally suited for components of chemical sensors. Hence, it is not surprising that gas sensors made from individual nanotubes show good sensitivities at room temperature,[55] in comparison to commercially available classical semiconductor sensors, which in general operate above 200°C. However, a necessary prerequisite is that the molecules to be detected must have a distinct electron donating or accepting ability, which is fulfilled, for example, by ammonia (NH_3) as a donor and nitrogen dioxide (NO_2) as an acceptor. The adsorption of these molecules on the nanotubes is associated with a partial charge transfer, which alters the charge-carrier concentration or, alternatively, the adsorbed molecules may affect the potential barriers present at the tube–electrode contacts. In any event, the resulting change in the electrical resistance of the nanotube is utilized as a sensor signal. However, for the detection of molecules that are only weakly adsorbed (e.g., carbon monoxide and hydrogen), the change in resistance is often too small. A possible method to overcome this drawback is accomplished by the modification of the nanotube sidewalls with nanoparticles made of a suitable metal. For instance, sensitive hydrogen sensors operating at room tem-

perature can be obtained via the deposition of palladium nanoparticles either by direct evaporation[56] or through electrodeposition.[57] Electrodeposition offers the specific advantage of site-selectivity, since the metal decoration is restricted to the current-carrying tubes, so that the remaining substrate surface is unaffected. As an example, Figure 13 depicts the resistance change of a semiconducting SWCNT with electrodeposited Pd particles upon exposure to hydrogen. The operation mechanism is largely analogous to that of a palladium gate field-effect transistor realized within classical silicon technology.[58] Specifically, molecular hydrogen is split on the surface of a Pd particle into atomic hydrogen, which diffuses to the Pd/SWCNT interface. At this interface, a dipole layer is formed, which acts like a microscopic gate electrode that locally changes the charge-carrier concentration. It should be mentioned that the recovery of this type of room-temperature-operated hydrogen sensor requires a supply of oxygen to remove the hydrogen atoms in the form of water.

5.3. Electrochemical Sensors

Carbon nanotubes exhibit high electron transfer rates for different redox couples in various media,[59] which has stimulated an increasing amount of research into CNT-based amperometric sensors for the detection of specific analytes in solution. The length scales of CNTs are similar to that of typical biological molecules, which gives CNTs an edge over other materials in functioning as effective electrodes in bioelectrochemical sensing.[60] In particular, their high aspect ratio and their diameter in the nanometer range make CNTs particularly well suited for direct electrochemical communication with the redox site of a protein, without requiring any mediator. When properly arranged, a nano-
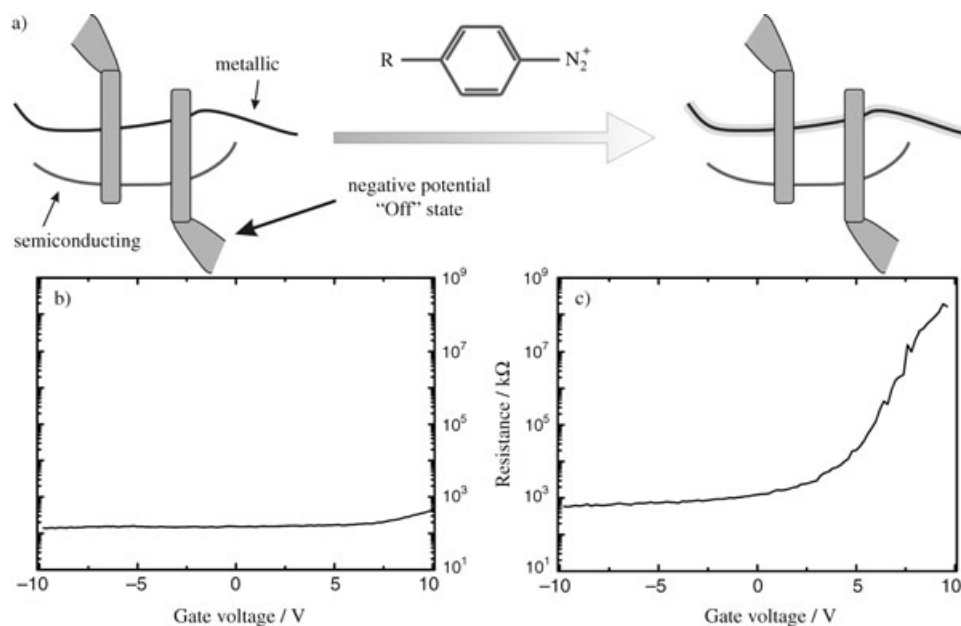

Figure 12. Selective ECM for the fabrication of a field-effect transistor starting from a sample containing both metallic and semiconducting nanotubes: a) Schematic of the fabrication concept. Gate dependence of room-temperature resistance before (b) and after (c) selective ECM.

tube should have the capability to act as a 1D channel that guides electrons towards the redox center. Direct electron transfer has been achieved with various types of CNT electrodes for cytochrome c,[61] horseradish peroxidase,[62] myoglobin,[63] as well as glucose oxidase.[60] It is noteworthy that in the latter case, the redox-active center is deeply embedded within the protein. In some cases, an oxidative pretreatment that introduces negatively charged surface groups on the CNTs was necessary to achieve high electron transfer rates. In a strategy to optimize the accessibility of the redox center, aligned CNT arrays have been fabricated using self-assembly techniques, followed by the covalent attachment of microperoxidase to the tube ends.[64] On this basis, various types of amperometric biosensors have been fabricated.[65] Figure 14 schematically illustrates the working principle of a glucose sensor obtained by immobilizing glucose oxidase onto SWCNTs deposited on a glassy carbon surface.[66]
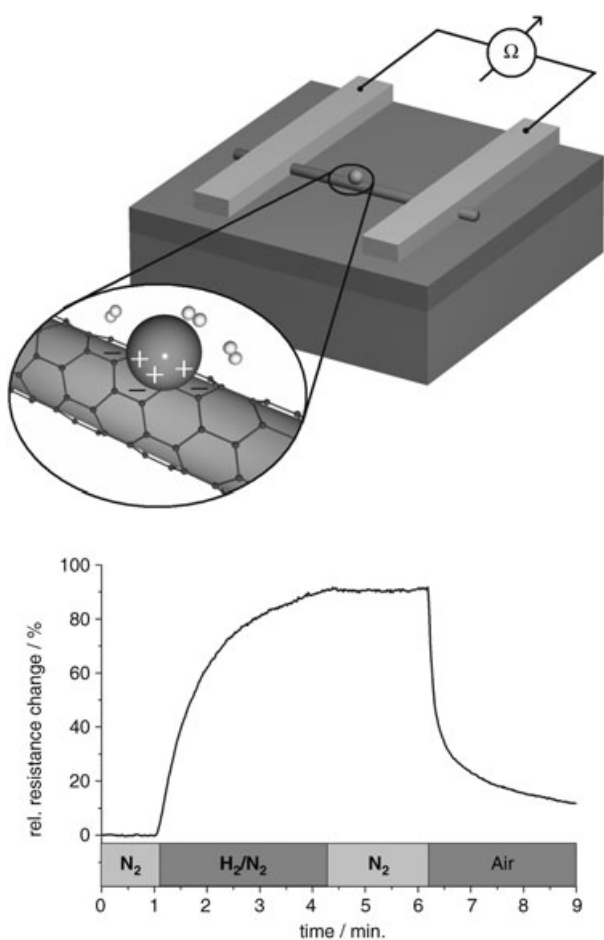

Figure 13. a) Fabrication of a hydrogen sensor from a nanotube decorated with palladium nanoparticles; b) change in electrical resistance of the sensor upon contact with hydrogen at room temperature.

5.4. Heterogeneous Catalysis

For a long time, active carbon has found widespread application as a support material in heterogeneous catalysis. Compared to this form of carbon, carbon nanotubes offer
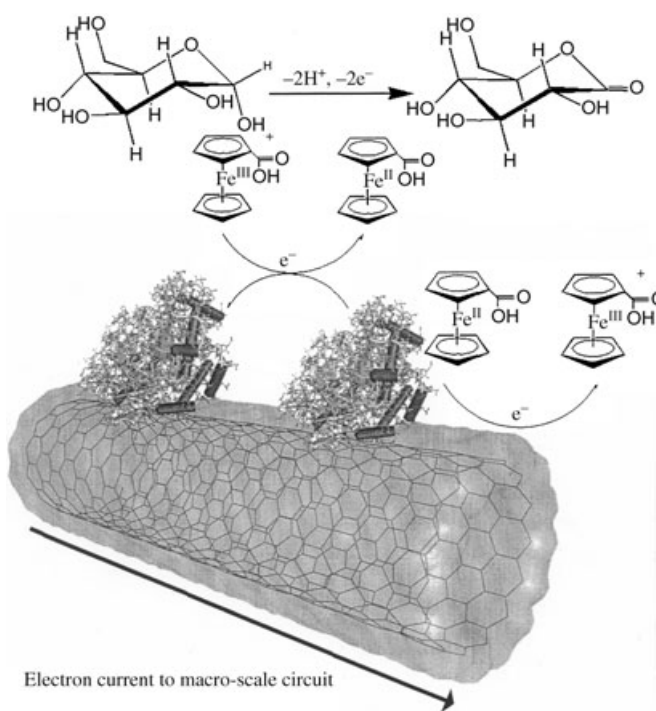

Figure 14. Bio-electrochemical sensing with carbon nanotubes: Schematic showing the operation mechanism of a SWCNT-based amperometric glucose sensor. The presence of glucose is sensed by SWCNTs modified with glucose oxidase (adapted from ref. [66]).

the advantage of a more defined morphology and chemical composition as well as the possibility to attach catalysts onto their surface through covalent bonds. The applicability of SWCNTs as carriers for catalytically active molecular functional units has recently been demonstrated through the covalent coupling of an organic vanadyl complex.[67] The nanotubes modified in this manner (see Figure 15) permit the catalytic cyanosilylation of aldehydes.

5.5. Mechanically Reinforced Composites

Carbon nanotubes possess extraordinarily high tensile strength, which outreaches that of a steel wire of corresponding thickness by around one order of magnitude. This attribute combined with their high length-to-diameter ratio and low density (one-sixth that of steel) makes CNTs valuable components for mechanically reinforced composite materials. A critical issue here is the attainment of good adhesion between the matrix and the individual tubes, which is required for an effective transfer of the mechanical load onto the nanotubes. To this end, covalent coupling between the matrix and the nanotubes is currently under extensive investigation. An optimal density of covalently bonded groups on the nanotubes would ensure that sufficient linkages to the matrix are provided without impeding too much the mechanical stability of the nanotubes. A promising approach for the reinforcement of organic polymers comprises of polymer synthesis from covalently attached initiator sites. In this manner, the radical polymerization of methacrylate
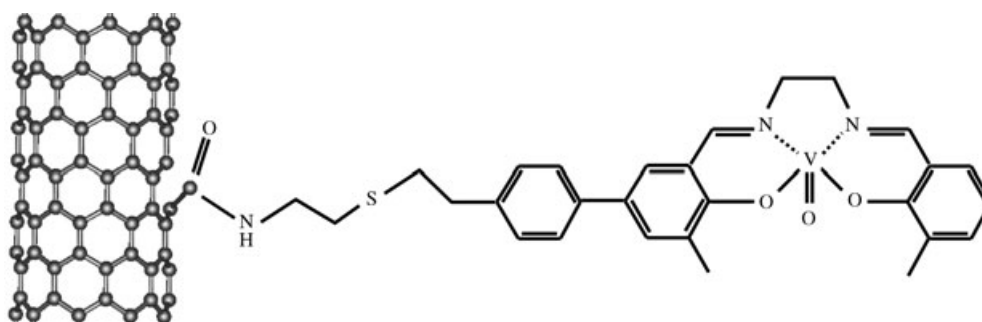
Figure 15. SWCNT with a covalently bonded vanadyl complex for applications in catalysis.
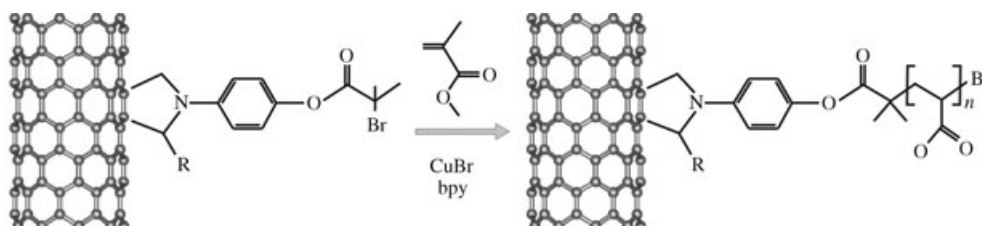

Figure 16. Polymerization of a methacrylate ester from an initiator site that is covalently attached to the nanotube sidewall.

esters on the nanotubes has been realized (Figure 16).[68] This flexible "grafting-from" approach has recently been extended to ring-opening metathesis polymerization reactions, in which SWCNTs were functionalized with ruthenium-based catalysts.[69]

6. Conclusion and Outlook

Carbon nanotubes are nowadays commonly used in laboratories due to their commercial availability in large quantities. In addition, effective purification methods can ensure a reasonable quality of the samples. The recently developed chemical and electrochemical functionalization schemes have significantly extended the application spectrum of CNTs. However, only little is known about the structure of the functionalized nanotubes at the atomic scale. Very recent investigations have used scanning tunneling microscopy (STM)[70] to learn more on this aspect, due to the proven capability of this method to record atomically resolved images of bare SWCNTs and the structural defects contained therein.[71] Despite these efforts, the unequivocal imaging of individual functional groups located on the sidewall of SWCNTs still remains to be demonstrated. Although some signatures of covalently attached functional groups have been reported, the interpretation of the STM images is often complicated by possible artifacts when substrates such as highly oriented pyrolytic graphite (HOPG) are used.[70] In the future, a better knowledge of the density and distribution of attached functional moieties will also help to deepen our understanding of the dependence of chemical reactivity on the detailed structure of the nanotubes. On this basis, various types of nanoscale electrical devices fabricated by controlled local covalent functionalization of SWCNTs, such as molecular diodes[72] or single-electron transistors[73] may be accessible in a more controlled manner.

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