Part I 3-D Carbon-rich  $\pi$ -Systems – Nanotubes and Segments

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\*A List of Abbreviations can be found at the end of this chapter.

# 1.1 Introduction to Carbon Nanotubes – A New Carbon Allotrope

Carbon nanotubes (CNTs) are cylindrically shaped macromolecules consisting of graphene-structured carbon atoms with diameters from 1.5 to 10 nm and lengths ranging from 1 to several hundred  $\mu$ m [1]. The small tubules appear as concentrically nested multi-walled carbon nanotubes (MWCNTs) or as a single layer of carbon atoms, the single-walled carbon nanotubes (SWCNTs). Both MWCNTs and SWCNTs can be grown in tangled structures or ordered close-packed struc-



**Fig. 1.1** Idealized representation of different structures of defect-free and opened carbon nanotubes: (a) concentric MWCNT; (b) "metallic" armchair [10,10] SWCNT; (c) helical

chiral semiconducting SWCNT; (d) zigzag [15,0] SWCNT; (e) SWCNT bundle. The armchair (b) and zigzag tubes (d) are achiral.

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tures. As a consequence, within the SWCNTs achiral zigzag and armchair tubes and helical chiral nanotubes have to be distinguished because of different "rollings" of the graphene sheet into a cylinder (Fig. 1.1). SWCNTs typically exist as ropes or bundles of individual tubes.

Because of their diverse structure, one-third of the tubes are expected to possess metallic character and the remaining two-thirds to behave as semiconductors [2, 3]. CNTs represent potential candidates to be used in field emission [4–6] and nanoelectrical devices [6–10], components of electrochemical energy [11, 12] and hydrogen storage systems [13, 14] and as components in composite materials [15–17]. They represent the ultimate carbon fiber, exhibiting exceptional mechanical properties [18–21] by being up to 100 times stronger than steel [22].

Since their discovery by Iijima in 1991 [23], carbon nanotubes have become the subject of intense research activities [2, 3]. Today they are widely recognized as *the* essential contributors to nanotechnology. However, their lack of solubility and their multidisperse dimensions present a considerable barrier towards processing and usage of their promising property profile for technological applications.

# 1.2 Functionalization of Carbon Nanotubes

Attaching chemical functionalities to CNTs can improve their solubility and allow for their manipulation and processability [24].The chemical functionalization can tailor the interactions of nanotubes with solvents, polymers and biopolymer matrices. Modified tubes may have physical or mechanical properties different from those of the original nanotubes and thus allow tuning of the chemistry and physics of carbon nanotubes. Chemical functionalization can be performed selectively, the metallic SWCNTs reacting faster than semiconducting tubes [25].

In dealing with functionalization, one has to distinguish between functionalization of SWCNTs and MWCNTs, between covalent and noncovalent functionalization, sidewall functionalization and defect functionalization, chemical functionallization, biofunctionalization and exohedral and endohedral functionalization (Fig. 1.2) [24]. Covalent functionalization is based on covalent linkage of functional entities onto the nanotube's carbon scaffold at the termini of the tubes or at their sidewalls. Covalent sidewall functionalization is associated with a change in hybridization from sp<sup>2</sup> to sp<sup>3</sup> and a loss of conjugation. Defect functionalization takes advantage of oxygenated sites and structural defects such as pentagon and heptagon irregularities in the hexagon graphene framework. Noncovalent functionalization is mainly based on supramolecular complexation. A special case of functionalization is the endohedral functionalization of CNTs, i.e. the filling of the tubes with atoms or small guest molecules.



Fig. 1.2 Different possibilities for the functionalization of SWCNTs: (a) noncovalent exohedral functionalization with polymers; (b) defect-group functionalization; (c) noncovalent exohedral functionalization with molecules through  $\pi$ -stacking; (d) sidewall functionalization; (e) endohedral functionalization, in this case C<sub>60</sub>@SWCNT.

# 1.3 Covalent Functionalization

Addition chemistry has developed into a promising tool for the modification and derivatization of the surface of nanotubes [24, 26]. However, it is difficult to achieve chemoselectivity and regioselectivity control of addition reactions, requiring hot addends such as arynes, carbenes, radicals, nitrenes or halogens under drastic reaction conditions.

# 1.3.1 Halogenation of Carbon Nanotubes

# 1.3.1.1 Fluorination of Carbon Nanotubes

Because of the low reactivity of the surface of CNTs, fluorination was taken into consideration as one of the first sidewall functionalization reactions [27]. Fluorine as the most electronegative element in its elemental form is a powerful oxidizer. Mickelson et al. reported in 1998 extensive controlled and nondestructive sidewall fluorination of SWCNTs (Fig. 1.3) [28]. The functionalized F-SWCNTs dissolved well in alcohol and gave long-living metastable solutions [29].

Most of the experimental work on fluorination has been performed using elemental fluorine diluted in an inert gas at elevated temperatures [28, 30, 31]. Comparative fluorination of open- and closed-end SWCNTs was performed with ele-



Fig. 1.3 Schematic depiction of a sidewall fluorinated SWCNT.

mental fluorine gas and the structural changes of the tubes were investigated [32]. Using iodine pentafluoride (IF<sub>5</sub>), the highest degree of fluorination with a composition of about CF was achieved [33]. Low-temperature plasma processes do not involve the use of wet chemicals or exposure of the tubes to high temperature and generate very little chemical residue [34]. Recently, SWCNTs have been functionalized using CF<sub>4</sub> [35] or a CF<sub>4</sub> or SF<sub>6</sub> plasma produced by reactive ion etching (RIE) [36]. The surface of aligned MWCNT arrays was modified by a CF<sub>4</sub> RIE-plasma treatment and the effect on the field emission properties of the aligned MWCNT films was studied [34]. CF<sub>4</sub> microwave discharge was used to F-functionalize SWCNTs and the samples were characterized through spectroscopy, scanning electron microscopy (SEM) and X-ray methods [37]. A low-level fluorination of MWCNTs was achieved at ambient temperature under the influence of light using  $XeF_2$  as the fluorine source [38]. An atmosphere of trifluoromethane or hexafluoropropene served as the functionalizing medium during ball-milling of SWCNTs at room temperature. Thus, F-SWCNTs with 0.3-3.5 wt.% of fluorine were obtained [39].

The major disadvantage of fluorine-functionalization is the high degree of addition of fluorine atoms, reflecting a great number of tube defects. Furthermore, the fluorinated material exhibits significant changes in spectroscopic properties, providing evidence for electronic perturbation. Fluorination results in a modification of the electronic structures of the tubes and changes the electrical resistance depending on the coverage and method of fluorine application. For fluorinated SWCNTs, evidence was shown for exfoliation of nanotube ropes and bundles into individual tubes. F-SWCNTs were found to be "cut" at the fluorinated sites during pyrolysis [40]. Especially for the production of composite materials, F-SWCNTs seem to be a rather promising material.

The fluorotubes are very soluble and open new routes to solution-phase chemistry. F-SWCNTs can serve as a starting material for a wide variety of chemical sidewall functionalizations (see Section 1.3.1.4). By treatment with hydrazine or LiBH<sub>4</sub>–LiAlH<sub>4</sub>, the majority of the covalently bound fluorine could be removed (Scheme 1.1) [29, 41], restoring most of the conductivity and spectroscopic properties of the pristine material.



**Scheme 1.1** Removal of covalently bound fluorine by treatment with hydrazine or lithium borohydride–lithium aluminum hydride.

# 1.3.1.2 Chlorination of Carbon Nanotubes

Electrolytic functionalization of MWCNTs succeeded with evolution of chlorine on an anode made from a foil of carbon nanotubes. Furthermore, oxygen-bearing functional groups such as hydroxyl and carboxyl are formed at the same time, enhancing the solvation of the tubes in water or alcohol [42]. Using another technique of functionalization, from ball-milling of purified MWCNTs in the presence of Cl<sub>2</sub> as reactant gas, cleavage of the tubes' C-C bonds and breaking of the tubes occurred and Cl-functionalized tubes were obtained [43]. Recently, Cl-SWCNTs were prepared by chemical vapor deposition of CHCl<sub>3</sub> or Cl<sub>2</sub>C=CCl<sub>2</sub> and subsequent radical addition of chlorine atoms under ball-milling conditions at room temperature. This kind of functionalized tubes were estimated to contain 5.5– 17.5 wt. % of chlorine [39]. A theoretical suggestion for controlled functionalization of SWCNTs with chlorine was presented by Fagan et al. in 2003 [44]. The idea was to substitute carbon network atoms of nanotubes by inserting Si atoms, thus gaining an sp<sup>3</sup>-like stable defect center as trapping site for the chemisorption of other atoms or molecules. Because of the experimental evidence about the possibility of substitutional doping of fullerenes by Si atoms, it is conceivable to dope CNTs similarly with Si [44].

# 1.3.1.3 Bromination of MWCNTs

The low susceptibility of CNTs to bromination was utilized as a means of purification for MWCNTs contaminated by other carbon particles [45, 46].

### 1.3.1.4 Chemical Derivatization of "Fluoronanotubes"

By treating fluoronanotubes with strong nucleophiles such as Grignard reagents, alkyl- and aryllithium reagents, metal alkoxides, acyl peroxides, amines and diamines, the fluorine atoms can be replaced through substitution [29, 47–50].



**Scheme 1.2** Treatment of fluorinated tubes with strong nucleophiles and replacement of the fluorine substituents, leading to deriva-

tized alkyl- and alkoxyl-nanotubes and aminofunctionalized nanotubes as products.

Derivatized products such as alkyl-, aryl-, alkoxyl- and amino-nanotubes and cross-linked nanotubes are obtained (Scheme 1.2). F-SWCNTs prepared by the HiPCO process exhibited a higher degree of alkylation using alkyllithium reagents than fluorinated SWCNTs from the laser-oven method. Dealkylation occurred at 500 °C. 1-Butene and *n*-butane were formed during the thermolysis [51]. A number of OH group-terminated SWCNTs have been prepared by fluorine displacement reactions of F-SWCNTs with a series of diols and glycerol in the presence of alkali or with amino alcohols in the presence of pyridine as catalyst [52]. F-SWCNTs can be efficiently defluorinated with anhydrous hydrazine [29, 41, 48].

### 1.3.2

### **Oxidation of CNTs – Oxidative Purification**

### 1.3.2.1 Carboxylation of CNTs

One of the milestones in nanotube chemistry was the "oxidative purification" of carbon nanotubes by liquid- or gas-phase oxidation. This leads to opening of the tubes' caps, formation of defects in the sidewalls and introduction of oxygen-bearing functionalities into the tubes [24]. Oxidation ("purification") was achieved applying boiling nitric acid [53, 54], sulfuric acid [54] or mixtures of both [55], "piranha" (sulfuric acid–hydrogen peroxide) [56] or gaseous oxygen [57, 58], ozone [59–62] or air as oxidant [63–65] at elevated temperatures or combinations of nitric acid and air oxidation [66]. Other oxidants used to functionalize CNTs are superacid HF–BF<sub>3</sub>, OsO<sub>4</sub> and RuO<sub>4</sub>, OsO<sub>4</sub>–NaIO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, KMnO<sub>4</sub> plus phase-transfer catalyst (PTC), etc. [67–70]. The aim of this oxidative treatment, drawing its inspiration from well-known graphite chemistry [71, 72], is the oxidative removal of metal catalyst particles used in the synthesis of the tubes and of amorphous carbon as a synthesis byproduct [56].

Upon oxidative treatment, the introduction of carboxylic groups and other oxygen-bearing groups at the end of the tubes and at defect sites is promoted, decorating the tubes with a somewhat indeterminate number of oxygenated functionalities. However, because of the large aspect ratio of CNTs, considerable sidewall functionalization also takes place (Fig. 1.4). HNO<sub>3</sub> oxidation in combination with column chromatography and vacuum filtration led to a new purification method for SWCNTs, developed by Hirsch's group [53]. The oxidative treatment introduces defects on the nanotube surface [73], oxidizes the carbon nanotubes ("hole doping") and produces impurity states at the Fermi level of the tubes [74]. In addition to purifying the raw material by removal of impurities, oxidation can be used to cut ("etch"), shorten and open the CNTs [56, 75-78]. Cutting and shortening depend on the extent of the reaction and give rise to a new length distribution which can be determined by transmission electron microscopy (TEM). The cutting results in SWCNTs with open and oxygenated ends; the degree of oxygenated functionalities were determined spectroscopically [59, 60]. Since chemical reactivity is a function of curvature [79], the oxidative stability also depends on the tube diameter [49, 80]. Mawhinney et al. [59] showed that with 1.4 nm diameter



Fig. 1.4 Section of an oxidized SWCNT, reflecting terminal and sidewall oxidation.

SWNTs, room-temperature oxidation by ozone is confined to the end caps and to dangling bonds created by removal of the caps. A detailed study of diameter-dependent oxidative stability by Zhou et al. [80] recently confirmed a direct relationship between diameter and reactivity. Using the resonance-enhanced Raman radial breathing mode, the authors clearly showed that smaller diameter tubes are more rapidly air oxidized than larger diameter tubes [71]. In their review on the covalent chemistry of SWCNTs [24d], Bahr and Tour reported that the HiPCO process produced smaller diameter SWCNTs (*ca.* 0.7 nm) were more reactive towards ozone than larger diameter SWNTs formed by laser ablation. This allows for enrichment of large-diameter single-walled carbon nanotubes by using a mixed concentrated  $H_2SO_4$ –HNO<sub>3</sub> treatment [81].

Solution-phase mid-IR spectroscopy was used to assess the amount of functionality introduced into SWNTs by oxidation. For a [10, 10] SWNT containing 40 carbon atoms in the unit cell, 20 carboxylic acid groups at each end of the tubes were found. A perfect 100 nm long [10, 10] SWNT-COOH contains approximately 16 000 C atoms [40 × (1000/2.46)] and 40 carboxylic acid groups [82]. Zhang et al. [83] claim to have improved the efficiency of nanotube oxidation and functionalization by using KMnO<sub>4</sub> as oxidant and a PTC. A comparison between KMnO<sub>4</sub> oxidation with or without PTC resulted in a yield of about 35–40% of functionalized tubes/total weight for the reaction without PTC. For the PTC-catalyzed reaction, the yield of functionalized nanotubes was about 65–70%. However, PTC-functionalized CNTs displayed a higher concentration of –OH groups (~23%) and ~3.8% of –COOH groups only [83].

SWNTs oxidized by either acid or ozone treatment have been assembled on a number of surfaces, including silver [84], highly-oriented pyrolytic graphite (HOPG) [85] and silicon [86]. Heavily oxygenated ozonized SWCNTs have been used as ligands for the growth of CdSe and CdTe quantum dots, leading to the formation of nanotube–nanocrystal assemblies [87, 88]. To mitigate the problem of poor matrix-SWCNT connectivity and phase segregation in polymer–SWCNT hybrid materials, acid-treated oxidized and negatively charged SWCNTs were assembled layer-by-layer (LBL) with positively charged poly(ethylenimine) (PEI) polyelectrolyte [89]. After subsequent chemical cross-linking, a nanometer-scale composite with SWCNT loadings as high as 50 wt.% could be obtained with a tensile strength approaching that of ceramics [89].

SWCNT films (bucky paper) have been prepared using aqueous dispersions of SWCNTs containing 0, 3, 6 and 10 M nitric acid. With increasing acid concentra-

tion, the film tensile strength increased from 10 to 74 MPa and the tensile modulus from 0.8 to 5.0 GPa, whereas the d.c. electrical conductivity decreased [90]. The effect of oxidation time and ultrasonication on MWCNTs, the concentration of carboxylic groups being measured by potentiometric titration, was investigated [91]. A sonochemical treatment to promote the density of surface functional groups of MWCNTs was successfully employed during oxidation [92]. Distinctive direct sidewall functionalization of MWCNTs has been carried out using dilute nitric acid under supercritical water (SCW) conditions. The functionalization proceeded invasively from the outer to the inner graphitic layers of the MWCNTs, the resulting material being comprised of a functionalized amorphous carbon sheath covering the remaining inner nanotube [93]. Recently, the electrical conductivity of MWCNT-epoxy composites was investigated with respect to the oxidative treatment of the original MWCNTs [94]. Oxidized aligned MWCNT arrays, grown by chemical vapor deposition (CVD) on a platinum substrate and acid or air treated, were used to immobilize the enzyme glucose oxidase [95]. The enzyme immobilization allows for direct electron transfer from the enzyme to the transducer and can be used as an amperometric biosensor (cf. Section 1.3.7.4), to record electrically the conversion of glucose to gluconic acid [95].

## 1.3.2.2 Defect Functionalization – Transformation of Carboxylic Functions

## Amidation - formation of CNT-carboxamides

The oxidative introduction of carboxylic functions to nanotubes provides a large number of CNT-functional exploitations and permits covalent functionalization by the formation of amide and ester linkages and other carboxyl derivatives [24]. Bifunctional molecules (diamines, diols, etc.) are often utilized as linkers. More illustrative examples are nanotubes decorated with amino-functionalized dendrimers, nucleic acids, enzymes, etc., and the formation of bioconjugates of CNTs [96].





occur at defect sites along the sidewalls; also other functionalities such as esters, quinones and anhydrides are formed. (b) DCC as coupling reagent. CNT-carboxamides are conventionally obtained by amidation of CNT-acyl chlorides, derived from the reaction of carboxylated tubes with thionyl chloride [56, 97]. Similarly, carboxamide nanotubes have been prepared using dicyclohexylcarbodiimide (DCC) as condensing agent and allowing for the direct coupling of amines and carboxylic functions under neutral conditions (Scheme 1.3) [98, 99].

Haddon and coworkers were the first to report the functionalization of oxidatively treated SWCNTs with alkylamines and aniline derivatives [97, 100]. The conversion of the acid functionality to the *N*-octadecylamide led to the first shortened soluble SWCNTs [97]. The analysis of octadecylamido (ODA)-functionalized SWCNTs by solution-phase mid-IR spectroscopy gave about 50 wt. % of the acylamide functionality [101]. Tethering of a series of primary and secondary achiral and chiral amines, ranging from myrtanylamine to various nitroanilines, with SWCNTs and also covalent functionalization of SWCNTs with lipase enzymes was achieved by Wang et al. [102]. Functionalization of SWCNTs with *N*-(1-pyrenylmethyl)-1,5-diaminopentane resulted in the formation of pyrene-substituted SWCNT derivatives, the photochemical properties of which were studied by quenching experiments and laser flash photolysis [103]. Water solubilization of SWCNTs was achieved by amidation of SWCNT-COCl with glucosamine. Their solubility ranged from 0.1 to 0.3 mg mL<sup>-1</sup> [104].

The reaction between toluene 2,4-diisocyanate and carboxylated MWCNTs afforded amido-functionalized nanotubes containing highly reactive isocyanate groups on their surface (Scheme 1.4). The amount of the isocyanate groups was determined by chemical titration and thermogravimetric analysis (TGA) [105]. The modified tubes may constitute promising components to prepare polymer–nanotube composites and coatings [106].

Exposure of CNT-acyl chlorides to  $H_2N(CH_2)_{11}SH$  produced an amide linkage of the nanotubes to the alkanethiol [51]. Although the more nucleophilic thiols would be expected predominately to form thioesters, free thiols were shown to exist by atomic force microscopy (AFM) imaging of attached 10-nm gold nanoparticles [51]. Similarly, Liu et al. [107] achieved the thiolation of SWCNT pipes by reacting cysteamine [HS(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>] with carboxyl-terminated nanotubes under carbodiimide conditions yielding CNT–CONH(CH<sub>2</sub>)<sub>2</sub>SH. The functionalized tubes could be assembled as monolayers on a gold surface via Au–S chemical bonding (Scheme 1.5) [107].



**Scheme 1.4** Amido-functionalized CNTs containing highly reactive isocyanate groups at the tube surface.



**Scheme 1.5** Schematic diagrams of (a) the thiolization reaction of carboxyl-terminated CNTs with cysteamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH)

and (b) the assembling structure of SWCNTs on gold.

Newkome-type dendrons were attached to the carbon scaffold of SWCNTs and MWCNTs by defect group functionalization [108]. First- and second-generation amine dendrons such as those depicted in Fig. 1.5 were condensed with the carboxyl groups of purified and opened SWCNTs and MWCNTs according to the carbodiimide technique [108]. These CNT derivatives can be expected to combine the characteristics of carbon nanotubes with those of dendrimers, potential building blocks for supramolecular, self-assembling and interphase systems.

Upon reacting SWCNT-acyl chlorides with  $\alpha$ , $\omega$ -diamines such as tripropylenetetramine as molecular linker and subsequent diamide formation with another SWCNT, Roth and coworkers [109, 110] and Kiricsi et al. [111] succeeded in the interconnection of tubes and the formation of carbon nanotube junctions. Endto-end (Scheme 1.6a) and end-to-side nanotube interconnections (Scheme 1.6b) were formed and observed by AFM. Statistical analyses of the AFM images showed around 30% junctions in functionalized material [42].

A gas-phase derivatization procedure was employed for direct amidization of oxidized SWCNTs with simple aliphatic amines. In some cases a minor amount



Fig. 1.5 Modification of oxidized CNTs with Newkome-type amino dendrimers.



**Scheme 1.6** Preparation of carboxamide junctions between SWCNTs: (a) end-to-end junctions and (b) sidewall-to-end junction between individual tubes.



**Scheme 1.7** Gas-phase amidation of oxidatively purified SWCNTs with octadecylamine (ODA) to obtain zwitterionic functionalization products.

of chemically formed amides in addition to a larger portion of physisorbed amines was observed [112]. Full-length oxidatively purified SWCNTs were rendered soluble in common organic solvents by noncovalent (zwitterionic) functionalization (Scheme 1.7) in high yield [100, 113]. About 4–8% of the SWCNT C-atoms can be functionalized by octadecyl amine in this way [100, 113, 114], offering a simple route to solubilize SWCNTs.

AFM micrographs showed that the majority of the thick SWCNT rope bundles were exfoliated into small ropes (diameter 2–5 nm) and individual nanotubes with lengths of several micrometers during the dissolution process. Multiwavelength laser Raman scattering spectroscopy and solution-phase IR spectroscopy were used to characterize the library of SWCNTs produced in current preparations. The average diameter of metallic tubes was found to be smaller than that of semiconducting nanotubes in the various types of preparations [112]. Such zwitterion-functionalized SWCNTs were length-separated and size-fractioned by gel permeation chromatography (GPC) by Chattopadhyay et al. [115], AFM being the method to determine the length distribution/fraction.

HiPCO-SWCNTs were oxidized in a UV–O<sub>3</sub> gas–solid interface reaction and subsequently assembled on a rigid oligo(phenylenethynylene) self-assembled monolayer (SAM). In a "chemical assembly", based on condensation between the carboxylic acid functionalities of the O<sub>3</sub>-oxidized SWNTs and the amine functionalities of the SAMs, SWCNT-amides were formed in ordered arrays [116].

Carboxylic groups positioned at the open ends of SWCNTs were coupled to amines to form AFM probes with basic or hydrophobic functionalities by Wong et al. [117] (Scheme 1.8). Force titrations recorded between the ends of the SWCNT–AFM tips and hydroxy-terminated SAMs confirmed the chemical sensitivity and robustness of the AFM tips. Images recorded on patterned SAM allowed real molecular-resolution imaging [117].

4 1 Functionalization of Carbon Nanotubes



**Scheme 1.8** Schematic illustration of an SWCNT force microscope probe and modification of an oxidized SWCNT tip by coupling an amine RNH<sub>2</sub> to a terminal –COOH. The

probe is able to sense specific interactions between the functional group R and surface -OH groups.

With the amido functionalization, also new routes were opened to the covalent linkage of oligomers and polymers, dendrimers, peptides and biopolymers and to the formation of bioconjugates of carbon nanotubes.  $\alpha, \omega$ -Diaminopoly(ethylene glycol) and long-chain ethers of hydroxyaniline were attached to CNTs via amide bonds [118, 119]. Poly(ethylene glycol) (PEG) was grafted to shortened SWCNTs by SOCl<sub>2</sub> activation and amidation with PEG-monoamine [120]. Monoamino-terminated poly(ethylene oxide) (PEO) was grafted onto SWCNTs by amide formation of SWCNT-COCl and the aggregation behavior of the PEO-SWCNTs was investigated in solution and as Langmuir-Blodgett (LB) films [121]. Amino-terminated polystyrene (PS) was grafted onto oxidatively cut nanotubes via amide formation [122], purified MWCNTs were covalently functionalized with the amino copolymer poly(propionylethyleneimine-co-ethylenimine) by amidation of CNT-carbonyl chlorides and by heating CNT-carboxylic acids in the presence of the amino polymer, respectively [123]. A multifunctionalized nanotube was used by Holzinger et al. as the core in the synthesis of first-, secondand third-generation Frechet- and Newkome-type dendrimers, using DCC and water-soluble EDC as condensing agents [124]. Nanotubes were functionalized by bovine serum albumin (BSA) via diimide-activated amidation; the BSA conjugates obtained were highly water soluble [125, 126]. Results from characterizations showed intimate association with the tubes and the bioactivity of the CNT–BSA conjugate was proven by a protein microdetection assay [125]. Research is under way to investigate the biocompatibility of chemically inert carbon nanotubes by immobilization of biopolymers and proteins at the tubes. The protein transferrin, tagged with a fluorescent label, was immobilized by covalent amide formation with CNT-COOHs in the presence of carbodiimide EDC and sulfo-N-hydroxysuccinimide (sulfo-NHS) [127]. Amino-terminated DNA strands were used to functionalize the open ends and defect sites of oxidized SWCNTs [128].



**Scheme 1.9** Schematic representation of the enhanced electrochemical detection of DNA hybridization based on an MWCNT-COOH constructed DNA biosensor.

Haxani et al. reported carbodiimide-assisted amidation of SWCNT-COOHs with oligonucleotides and the preparation of a highly water-soluble adduct. Fluorescence imaging of individual nanotube bundles showed that the SWCNT-DNA adducts hybridized selectively with complementary strands [129]. A multistep route to the formation of covalently linked SWCNTs and DNA oligonucleotides was developed by Baker et al. and the covalent linkage proven by X-ray photoemission spectroscopy (XPS) [130]. The nanoscience group from Delft University had developed a technique to couple SWCNTs covalently to peptide nucleic acids (PNA), an uncharged DNA analog, and to hybridize the conjugate with complementary DNA. The recognition properties imparted to SWCNTs by oligonucleotide adducts could be used to program the attachment of CNTs to each other and to substrate features on which monolayers of complementary sequences are self-assembled [131]. From oxidized MWCNT-COOHs a glassy carbon electrode (GCE) was fabricated. In the presence of a water-soluble coupling reagent, oligonucleotide probes with an amino group at the 5'-phosphate end were covalently attached, to be used as a DNA biosensor (Scheme 1.9). Nucleotide-hybridization was performed and the specific nucleotide assembly was detected with the redox intercalator daunomycin as indicator [132].

The reduction of the amido functions of amide-solubilized MWCNTs by LiAlH<sub>4</sub> afforded the corresponding hydroxy-substituted CNTs, confirmed by FT-IR and XPS studies [133]. No morphology change of the nanotubes after reduction could be observed by Raman spectroscopy [133].

### Esterification - formation of CNT-esters

Acyl chloride-functionalized SWCNTs are also susceptible to reactions with other nucleophiles, e.g. alcohols. Haddon's group reported the preparation of soluble ester-functionalized carbon nanotubes SWCNT-COO(CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub> (Fig. 1.6a) obtained by esterification with octadecanol [134]. The syntheses of soluble polymer-bound and dendritic ester-functionalized SWCNTs have been reported by Riggs et al. by attaching poly(vinyl acetate-*co*-vinyl alcohol) (Fig. 1.6b) [135] and hydrophilic and lipophilic dendron-type benzyl alcohols [119], respectively, to SWCNT-COCl (Fig. 1.6c). These functional groups could be removed under basic and acidic hydrolysis conditions and thus additional evidence for the nature of the attachment was provided [119, 136].

16 1 Functionalization of Carbon Nanotubes



**Fig. 1.6** (a) SWCNT-ester SWCNT-COO(CH<sub>2</sub>)<sub>17</sub>CH<sub>3</sub>; (b) ester from SWCNT-COOH and poly(vinyl acetate-*co*-vinyl alcohol); (c) dendritic-type benzyl alcohol ether.

Ester-functionalized MWCNTs with terminal thiol groups were synthesized by converting the sodium salt of oxidatively purified MWCNTs with 2-bromoethanethiol in the presence of a phase-transfer agent. Gold-nanoparticles have been successfully self-assembled on the MWCNT-COO(CH<sub>2</sub>)<sub>2</sub>SH tubes to fabricate nanocomposites [137]. Labeling of SWCNTs with fluorescence probes was accomplished via esterification of the tubes by oligomerically tethered pyrene derivatives. The fluorescence and fluorescence excitation results showed that the tethered pyrenes form "intramolecular" excimers by  $\pi$ - $\pi$ -interactions (Scheme 1.10). The pyrene monomer and excimer emissions were significantly quenched by the attached SWCNTs. The quenching was explained in terms of the nanotube serving as acceptor for excited-state energy transfer from the tethered pyrene moieties [138].



**Scheme 1.10** Labeling of SWCNTs with fluorescence probes via esterification by derivatized pyrenes and formation of "intertubulary" dimers and excimers by  $\pi$ - $\pi$  interactions.

1.3 Covalent Functionalization 1



**Scheme 1.11** Grafting of polymers via atom transfer radical polymerization (ATRP) using an ester linkage to oxidized MWCNTs. Formation of MWCNT-COCl, reaction with

ethylene glycol and with 2-bromo-2-methylpropionyl bromide and grafting polymerization with methyl methacrylate (MMA).

A general strategy for grafting of polymers from MWCNTs via atom transfer radical polymerization (ATRP) using an ester linkage to oxidized MWCNTs was described by researchers at Shanghai Jiao Tong University [139]. Four steps included the formation of MWCNT-COCl, reaction with ethylene glycol, subsequent reaction with 2-bromo-2-methylpropionyl bromide to initiate radical addition sites and finally grafting polymerization with methyl methacrylate (MMA) in the presence of CuBr–pentamethyldiethylenetriamine (PMDETA) (Scheme 1.11) [139]. Polymer brushes with SWCNTs as backbones were similarly synthesized by grafting *n*-butyl methacrylate with 2-hydroxyethyl 2'-bromopropionate-initiated SWCNTs and ATRP polymerization under CuCl–bipy catalysis [140].

The formation of covalently PEG-grafted SWCNT hybrid material was achieved by the reaction of SWCNT-COCl with hydroxyl-terminated PEG in various solvents. Two different self-assembling morphologies, depending on the quality of the solvent, were discovered by high-resolution transmission electron microscopy (HR-TEM) [141].

### Thiolation – formation of SWCNT-(CH<sub>2</sub>)<sub>n</sub>SH

In 2003, Lim et al. [142] succeeded in a direct thiolation of the open ends of SWCNTs via successive carboxylation ( $H_2SO_4$ -HNO<sub>3</sub>;  $H_2O_2$ - $H_2SO_4$ ; sonication), NaBH<sub>4</sub> reduction, chlorination with SOCl<sub>2</sub> and thiolation (Na<sub>2</sub>S-NaOH) (Scheme 1.12). The intermediates and the final products were verified by FT-IR and NMR spectroscopy [142].

The thiolated CNTs were adsorbed on micron-sized silver and gold particles and gold surfaces to study the interactions between the thiol groups and the noble



Scheme 1.12 Thiolation of CNTs by modification of carboxylated tubes.



**Fig. 1.7** Schematic representation of the vertical view image of the thiolated CNTs with thiol groups at both ends, binding to a gold surface. The flexible tube body of SWCNTs

allows the CNT to conform its geometry for maximum binding energy at the expense of the bending energy. The result is a "bow-type" bundle of the thiolated CNTs.

metals. The thiol-metal adhesion was studied by SEM, AFM, wavelength-dispersive electron spectroscopy and Raman spectroscopy. A new type of bonding between the CNT and a noble metal surface was proposed (Fig. 1.7) that involved a bow-type SWCNT with its two ends attached to the metal surface [142].

### Silylation of oxidized CNTs

A novel chemical functionalization method for MWCNTs through an oxidation and silylation process was reported in 2002. Purified and oxidatively functionalized MWCNTs were reacted with 3-mercaptopropyltrimethoxysilane, the CNT surface being joined to the organosilane moieties through OH groups [143]. Similarly, MWCNTs were functionalized by KMnO<sub>4</sub> oxidation under PTC catalysis and subsequent reaction with the hydrolysis product of 3-methacryloxypropyltrimethoxysilane (3-MPTS) (Scheme 1.13). The *O*-silyl-functionalized MWCNTs were characterized by FT-IR spectroscopy and energy-dispersive spectroscopy



**Scheme 1.13** Reaction of oxidatively functionalized MWCNTs with the hydrolysis product of 3-methacryloxypropyltrimethoxysilane (3-MPTS).

(EDS), SEM and TEM analysis [70]. The method allowed different organo-functional groups to be attached to MWCNTs, improving their compatibility with specific polymers for producing CNT-based composites.

A fluorinated octyltrichlorosilane was reacted with the carboxylic moieties of oxidized MWCNTs and, after reduction with the corresponding alcohol groups. The modification was confirmed by XPES and TGA [144].

# 1.3.3 Hydrogenation of Carbon Nanotubes

Several methods for the hydrogenation of SWCNTs have been described. Dissolved metals acted as the reducing agents. Chen et al. first reported the Birchlike reduction of SWCNTs using lithium in diaminoethane [79a]. TEM micrographs showed corrugation and disorder of the nanotube walls due to hydrogenation and the formation of C–H bonds was suggested. The average hydrogen content of SWCNTs after lithium–ammonia hydrogenation was determined by Pekker et al. from TGA/MS and corresponded to a composition of  $C_{11}$ H [145]. Hydrogenation occurred even on the inner tubes of MWCNTs, as shown by the chemical composition and the overall corrugation [145].

Owens and Iqbal [146] succeeded in an electrochemical hydrogenation of openended SWCNTs synthesized by CVD. Sheets of SWCNT bucky paper were used as the negative electrode in an electrochemical cell containing aqueous KOH solution as electrolyte. The authors claimed to have incorporated up to 6 wt.% of hydrogen into the tubes, determined by laser Raman IR spectroscopy and hydrogen release by thermolysis at 135 °C under TGA conditions [146]. However, the stability of exohydrogenated carbon nanotubes and the low temperature of hydrogen release at 135 °C [146] is contradictory with the 400–500 °C reported elsewhere [79a, 145].

Hydrogen bound to SWCNTs should not be released until *ca*. 500 °C, indicating robust attachment [145]. Theoretical first-principles total energy and electronic structure calculations of fully exohydrogenated zigzag and armchair SWCNTs ( $C_nH_n$ ) point to crucial differences in the electronic and atomic structures with respect to hydrogen storage and device applications.  $C_nH_n$ s were estimated to be stable up to a radius of a [8,8] CNT, with binding energies proportional to 1/*r*. By calculation, zigzag nanotubes were found to be more likely to be hydrogenated than armchair tubes with equal radius [147].

# 1.3.4 Addition of Radicals

Perfluorinated alkyl radicals, generated by photoinduction from heptadecafluorooctyl iodide, were added to SWCNTs and the perfluorooctyl-derivatized CNTs obtained (Scheme 1.14). No difference in the solubility of the fluoroalkyl-substituted nanotubes and the starting materials was observed [148]. A pathway to the radical functionalization of CNTs' sidewalls was predicted by classical molecular dy-



Scheme 1.14 Addition of heptadecafluorooctyl radicals obtained from irradiation of heptadecafluorooctyl iodide.



 $R = C_6 H_5$  and  $C_{11} H_{23}$ 

**Scheme 1.15** Functionalization of SWCNTs and fluorinated F-SWNTs with benzoyl ( $R = C_6H_5$ ) and lauroyl ( $R = C_{11}H_{23}$ ) peroxides.

namics simulations of the bombardment of a bundle of SWCNTs by CH<sub>3</sub> radicals [149].

Pristine SWCNTs and their fluorinated derivatives, F-SWCNTs, were reacted with organic peroxides to functionalize their sidewalls covalently by attachment of free radicals (Scheme 1.15). The tubes' reactivity towards radical addition was compared with that of corresponding polyaromatic and conjugated polyene  $\pi$ -systems [150, 151]. The characterization of the functionalized SWCNTs and F-SWCNTs was performed by Raman, FT-IR and UV/Vis/NIR spectroscopy and also by TGA/MS, TGA/FT-IR and with TEM measurements. The solution-phase UV/Vis/NIR spectra showed complete loss of the van Hove absorption band structure, typical of functionalized SWCNTs [150].

# 1.3.5

### Addition of Nucleophilic Carbenes

The reaction of a nucleophilic dipyridyl imidazolidene (DPI) with the electrophilic SWCNT  $\pi$ -system to give zwitterionic polyadducts was reported in 2001 by Holzinger et al. [148]. DPI was generated from the corresponding dipyridyl imidazolium system by deprotonation. Each covalently bound imidazolidene addend bears a positive charge, one negative charge/addend is transferred to the delocalized tube surface and a stable 14  $\pi$ -system is obtained (Scheme 1.16) [148].

Sufficiently derivatized nanotubes were soluble in DMSO, allowing the separation of insoluble, unreacted and insufficiently functionalized SWCNTs [148]. The n-doping of the tubes surface offers a new way to modify the tube properties and control the electronic properties.



Scheme 1.16 Sidewall functionalization by addition of nucleophilic dipyridyl imidazolidene to the electrophilic SWCNT π-system.

# 1.3.6 Sidewall Functionalization Through Electrophilic Addition

In 2002, Tagmatarchis et al. [152] reported the modification of SWCNTs through electrophilic addition of CHCl<sub>3</sub> in the presence of AlCl<sub>3</sub>. From hydrolysis of the so-produced labile chlorinated intermediate species, hydroxy-functionalized SWCNTs were obtained, the coupling of which with propionyl chloride led to the corresponding SWCNT propionate esters (Scheme 1.17) [152].



Scheme 1.17 Electrophilic addition of CHCl<sub>3</sub> to SWCNTs (i), followed by substitution of chlorine (ii) and esterification (iii): (i)  $CHCl_3$ ,  $AlCl_3$ ; (ii)  $OH^-$ , MeOH; (iii)  $C_2H_5COCl$ .

# 1.3.7 Functionalization Through Cycloadditions

### 1.3.7.1 Addition of Carbenes

In the course of a study on organic functionalization of CNTs, Haddon's group discovered in 1998 that dichlorocarbene was covalently bound to soluble SWCNTs (Scheme 1.18) [97]. Originally, the carbene was generated from chloroform with potassium hydroxide [79a] and later from phenyl(bromodichloromethyl)mercury [97]. However, the degree of functionalization was as low as 1.6 at.% of chlorine only, determined by XPS [153].





R = ethyl, tert-butyl, etc.

**Scheme 1.19** Sidewall functionalization of SWCNTs by [2+1]-cycloaddition of alkoxycarbonyl nitrenes obtained from azides.

# 1.3.7.2 Addition of Nitrenes

Sidewall functionalization of SWCNTs was achieved via the addition of reactive alkyloxycarbonyl nitrenes obtained from alkoxycarbonyl azides. The driving force for this reaction is the thermally-induced  $N_2$  extrusion. The nitrenes generated attack nanotube sidewalls in a [2+1]-cycloaddition forming an aziridine ring at the tubes sidewalls (Scheme 1.19).

With this technique, a broad range of aziridino-SWCNTs was obtained by our group by cycloadding addends such as alkyl chains, aromatic groups, crown ethers and oligoethylene glycol units (Fig. 1.8) [148, 154].

Nitrene additions led to a considerable increase in solubility in organic solvents; the highest solubility of 1.2 mg mL<sup>-1</sup> in DMSO and TCE was found for SWCNT ethylene glycol–crown ether adducts. AFM and TEM revealed that the formation



Fig. 1.8 Sidewall functionalization of SWCNTs via addition of (R)-oxycarbonyl nitrenes.



**Scheme 1.20** PEG-tethered SWCNTs and interconnections between individual SWCNTs through cycloaddition of  $\alpha$ , $\omega$ -polyethylene glycol dinitrenes as the molecular linker.

of thin bundles with typical diameters of 10 nm. The presence of the bundles in solution was supported by <sup>1</sup>H NMR spectroscopy; the elemental composition of the functionalized SWCNT was determined by XPS [155, 156]. The use of Raman and electron absorption spectroscopy (UV/Vis/NIR) showed that the electronic properties of the SWCNTs were mostly retained after functionalization, indicating less than 2 at.% addend per C-atom of the tube sidewalls [154]. Nitrene addition to nanotubes of different origins and production methods was compared with that to unfunctionalized pristine tubes by investigating their XPS, Raman and UV/Vis/NIR spectra and TEM images [155].

Tethered SWCNTs and interconnections between individual SWCNTs using  $\alpha, \omega$ -dinitrenes as the molecular linker (Scheme 1.20) were reported the first time in 2003 by Holzinger et al. [157]. The bisnitrenes were derived from thermolysis of poly(ethylene glycol) PEG 600 bisazidocarbonate; the covalent linkage was characterized by SEM studies, XPS, X-ray diffractograms and Raman spectra [157].



**Scheme 1.21** Schematic representation of the cyclopropanation of SWCNTs and the introduction of chemical markers for AFM visualization and <sup>19</sup>F NMR spectroscopy and XPS: (i) diethyl bromomalonate, DBU, room

temperature; (ii) 2-(methylthio)ethanol, diethyl ether; (iii) preformed 5-nm gold colloids; (iv) sodium or lithium salt of 1H,1H,2H,2H-perfluorodecan-1-ol.

# 1.3.7.3 Nucleophilic Cyclopropanation – Bingel Reaction

Fullerenes are known to react easily with bromomalonates in the Bingel reaction [158] to form cyclopropanated methanofullerenes [159]. The equivalent transformation was performed by Coleman et al. [160] with purified SWCNTs and diethyl bromomalonate as addend. They developed a chemical tagging technique which allows the functional groups to be visualized by AFM. The cyclopropanated methano-SWCNT derivatives were transesterified with 2-(methylthio)ethanol and the cyclopropane groups were "tagged" by exploiting gold–sulfur interactions using preformed 5-nm gold colloids (Scheme 1.21) [160].

Gold colloids were observed both on the sides and at the ends of the nanotubes, indicating sidewall and termini modification. To confirm further the derivatization of the SWNTs, a perfluorinated marker was introduced by transesterification to allow the nanotubes to be probed by <sup>19</sup>F NMR spectroscopy and XPS [160].

### 1.3.7.4 Azomethine Ylides

Prato and coworkers succeeded in the 1,3-dipolar addition of azomethine ylides to CNTs [161]. Treatment of pristine SWCNTs with an aldehyde and an *N*-substituted glycine derivative resulted in the formation of substituted pyrrolidine moieties on the SWCNT surface (Scheme 1.22). The approach works effectively with both SWCNTs, prepared by several different methods, and MWCNTs. The pyrrolidino-functionalized CNTs were sufficiently soluble in common organic solvents and were characterized by several spectroscopic techniques and TEM [161]. The



Scheme 1.22 1,3-Dipolar addition of azomethine ylides to SWCNTs and MWCNTs.

R<sup>2</sup>-CHO + R<sup>1</sup>-NHCH<sub>2</sub>COOH

azomethine ylide functionalization was also used to purify HiPCO SWCNTs from metal nanoparticles and carbon impurities [162].

The covalent functionalization of CNTs with azomethine ylides allows for a number of other functionalities to be immobilized onto the SWCNT surface [163]. Amidoferrocenyl-functionalized SWCNTs appeared to be efficient anion receptors for the redox recognition of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> [164]. A ferrocene-modified glycine precursor was used to functionalize the CNT sidewalls with ferrocene units (Fig. 1.9). A subsequent electron transfer was observed from ferrocene to the SWCNTs on photoexcitation, opening up ways to the use of ferrocene-SWCNT hybrids in solar energy applications [165]. Ferrocenyl-functionalized SWCNTs of that kind were coupled to glucose oxidase (GOx) within an amphiphilic polypyrrole matrix for the amperometric catalytic detection of glucose as a glucose biosensor [166].

Functionalized N-triethylene glycol pyrrolidino-CNTs (Fig. 1.10a) allowed electrochemistry and quantum chemical calculations to be carried out to investigate the bulk electronic properties [167]. Functionalization obviously modified the electronic state of pristine CNTs; however, some of the metallic character was retained and the overall electron density of states (DOS) was not strongly affected [167]. Pyrrolidino-SWCNTs and -MWCNTs bearing a free amino-terminal N-oligoethylene glycol moiety formed supramolecular associates with plasmid DNA through ionic interactions. The complexes were able to penetrate within cells. SWCNTs



Fig. 1.9 1,3-Dipolar cycloaddition of ferrocene-modified azomethine ylide to SWCNTs in order to functionalize CNT sidewalls with electron donor units.



**Fig. 1.10** (a) Functionalized *N*-(triethylene glycol)pyrrolidino-CNTs to carry out electrochemistry and quantum chemical calcula-

tions; (b) and (c) two types of cationically functionalized SWCNTs to bind with synthetic oligodeoxynucleotides.

complexed with plasmid DNA were able to allow for higher uptake of DNA and gene expression *in vitro* than could be achieved with individual DNA only [168]. The bindings of two types of cationically functionalized SWCNTs (Fig. 1.10b and c) with synthetic oligodeoxynucleotide (ODN) immunostimulatory CpG motif were compared by Bianco et al. [169]; the results demonstrated the potential of functionalized CNTs to enhance the immunostimulatory properties of ODN CpGs and the advantage for an effective delivery of ODN CpGs into target cells.

A series of amino acids, fluorescent probes and bioactive peptides have been covalently linked to functionalized CNTs through the terminal amino group of oligoethylene glycol functionalities (Fig. 1.10b). Using fragment condensation or selective chemical ligation of Cys-thiol groups, mono- and dipeptide-functionalized CNTs were obtained and their potential as drug delivery vehicles, for gene delivery and for delivery of antigens was evaluated [170].

### 1.3.7.5 [4+2]-Cycloaddition - Diels-Alder Reaction

The first Diels–Alder [4+2]-cycloaddition functionalization of CNTs has been reported recently [171]. Ester-functionalized SWCNTs were reacted with *o*-quinodimethane, generated *in situ* from benzo-1,2-oxathiin-2-oxide under microwave irradiation (Scheme 1.23). This technique opened up a new access to a novel family of modified carbon nanotubes.



**Scheme 1.23** Diels–Alder [4+2]-cycloaddition reaction of functionalized SWCNTs with *o*-quinodimethane under microwave irradiation.



**Scheme 1.24** (a) UV light-induced reversible sidewall osmylation of SWCNT and (b) electrical monitoring of the resistance at the single tube level.

### 1.3.7.6 Sidewall Osmylation of Individual SWCNTs

UV light-induced osmylation of carbon nanotubes was observed by exposure of SWCNTs to  $OsO_4$  vapor [172] and also in organic solvents (Scheme 1.24) [173].  $OsO_4$  addition to CNTs resulted in a pronounced increase in their electrical resistance by up to several orders of magnitude, which was electrically monitored at the individual tube level. The addition was reversible and the original resistance was restored [172]. The major products of osmylation in organic media were SWCNTs decorated with  $OsO_2$  particles, resulting in extended tube aggregation [173].

### 1.3.8

# Aryl Diazonium Chemistry - Electrochemical Modification of Nanotubes

Electrochemistry has become an elegant tool for the functionalization of CNTs. Applying a constant potential (potentiostatic) or a constant current (galvanostatic) to a CNT electrode immersed in a suitable reagent solution, highly reactive radical species can be generated. These reactive species readily functionalize CNTs or self-polymerize, forming a polymer coating of the tubes. In 2001, Tour's group grafted a series of phenyl functionalities by electrochemically coupling of aryldiazonium salts onto an SWCNT bucky paper electrode [174]. The reaction mechanism follows a one-electron reduction of the diazonium salt and subsequent addition of reactive aryl radicals (Scheme 1.25).



**Scheme 1.25** Grafting of phenyl functionalities on to a SWCNT bucky paper electrode by electrochemically coupling of aryldiazonium

salts; one-electron reduction of the diazonium salt and addition of aryl radicals.



Scheme 1.26. Solvent-free functionalization of carbon nanotubes performed with various substituted anilines and isoamyl nitrite or

NaNO<sub>2</sub>-acid. R can be Cl, Br, NO<sub>2</sub>, CO<sub>2</sub>CH<sub>3</sub>, alkyl, OH, alkylhydroxy, oligoethylene.

Based on TGA and elemental analysis, up to one in 20 nanotube carbons (5%) has been found to possess an aryl addend [174]. For the preparation of PS-CNT nanocomposites, the same authors functionalized SWCNTs by *in-situ* generation of a diazonium compound from 4-(10-hydroxydecyl)aminobenzoate [175]. From rheology data it was suggested that the reinforcement and dispersibility of the thus functionalized SWCNT-composites were improved over PS composites with pristine SWCNTs.

Basic studies on diazonium-CNT chemistry led to two very efficient techniques for SWCNT derivatization: solvent-free functionalization [176] and functionalization of individual (unbundled) nanotubes [175]. With the solvent-free functionalization (Scheme 1.26), heavily functionalized and soluble material is obtained and the nanotubes disperse in polymer more efficiently than pristine SWCNTs [176]. With the second method, aryldiazonium salts react efficiently with the individual (unbundled) HiPCO produced and sodium dodecyl sulfate (SDS)-coated SWCNTs in water. The resulting functionalized tubes (one addend in nine tube carbons) remained unbundled throughout their entire lengths and were incapable of reroping. [175].



**Scheme 1.27** Electrochemical modification of SWCNTs with aryldiazonium compounds: (a) reductive coupling of preformed *p*-nitrophenyldiazonium salts to SWCNTs and (b) anodic oxidation with *in situ*-generated dia-

zonium compounds from anilines. The dotted lines mark positions of further linkages that could be formed during the growth of a polymerized layer of phenyl units on the SWCNTs.



**Scheme 1.28** Electrochemical addressing of and subsequent linking with DNA forming an array of DNA–CNT hybrid nanostructures.

In 2002, Burghard and coworkers described an elegant method for the electrochemical modification of individual SWCNTs [177]. To address electrically individual SWCNTs and small bundles, the purified tubes were deposited on surfacemodified Si/SiO<sub>2</sub> substrates and subsequently contacted with electrodes, shaped by electron-beam lithography. The electrochemical functionalization was carried out in a miniaturized electrochemical cell. The electrochemical reduction was achieved by reduction of  $4-NO_2C_6H_4N_2^+BF_4^-$  in DMF with  $NBu_4^+BF_4^-$  as the electrolyte (Scheme 1.27a), anodic oxidation was accomplished with aromatic amines in dry ethanol with LiClO<sub>4</sub> as the electrolyte salt (Scheme 1.27b) [177].

Four different aryldiazonium salts have been used to functionalize SWCNTs through electrochemical reduction. By XPS and Raman diffusion measurements, the growth of aryl chains on the sidewalls of the nanotubes was observed [178]. Electrically addressable biomolecular functionalization of SWCNT electrodes and vertically aligned carbon nanofiber electrodes with DNA was achieved by electrochemically addressing (reduction) of nitrophenyl substituted nanotubes and nanofibers. Subsequently, the resulting amino functions were covalently linked to DNA forming an array of DNA–CNT hybrid nanostructures (Scheme 1.28) [179].

# 1.3.9 Reductive Alkylation and Arylation of Carbon Nanotubes

Reductive alkylation of carbon nanotubes using lithium and alkyl halides yields sidewall-functionalized nanotubes soluble in common organic solvents. Billups' group prepared dodecylated SWCNTs from raw HiPCO tubes using lithium and dodecyl iodide in liquid ammonia and demonstrated the occurrence of exten-



**Scheme 1.29** Reductive arylation of SWCNTs with iodobenzene derivatives, conversion to zwitterions by sulfonation.

sive debundling of the tubes [180]. Alkyl radicals were identified to be the intermediates in the alkylation step by GC/MS analysis of hydrocarbons formed as byproducts. Very recently, the same group reported the preparation of aryl-functionalized SWCNTs by treating SWCNTs with lithium in liquid NH<sub>3</sub> and subsequent reaction with aryl iodides (Scheme 1.29). Zwitterions were obtained from the aniline-derivatized SWCNTs by sulfonation, which were found to exhibit moderate solubility (50 mg  $L^{-1}$ ) in methanol [181].

## 1.3.10

# Addition of Carbanions - Reactions with Alkyllithium

Viswanathan et al. introduced carbanions onto SWCNT surfaces by treating the tubes with *sec*-butyllithium, providing initiating sites for the polymerization of styrene [182]. Recently, Chen et al. reported that on treating SWCNTs with *sec*-butyllithium and reacting the carbanions formed with  $CO_2$  under oxygen-free and anhydrous conditions, the SWCNTs were alkylated and carboxylated [183] (Scheme 1.30). The so-derivatized SWCNTs could be dispersed in water to give a nearly transparent solution of 0.5 mg mL<sup>-1</sup>; zeta potentiometric titrations indicated a feature similar to a zwitterionic polyelectrolyte [183].

MWCNTs have been functionalized with *n*-butyllithium by Blake et al. and subsequently the modified CNTs were covalently bonded to a chlorinated polypropylene [184]. The polypropylene-grafted MWCNTs were used to produce ultra-strong CNT polymer composites.



### SWCNT

**Scheme 1.30** Addition of carbanions, alkylation and carboxylation of SWCNTs: treatment with *sec*-butyllithium and subsequent reaction with CO<sub>2</sub>.

# 1.3.11 Covalent Functionalization by Polymerization – "Grafting To" and "Grafting From"

Grafting macromolecules to the tips and onto the convex walls of CNTs has been explored for several years, performed using the "grafting to" approach via reactions such as esterification and amidization [136, 185]. The "grafting from" approach has been employed to graft polymer chains onto solids from polymer-functionalized CNTs. PS was grafted from MWCNTs [186] and PS and PVK polymer chains were successfully grafted from the surface of SWCNTs using anionic polymerization [182, 187]. By ATRP, Gao et al. grafted covalently poly(methyl methacrylate) (PMMA) and PS onto MWCNTs [188]. Ejaz et al. successfully grafted polymer chains onto a solid surface [189]. Hao et al. grafted PS from the convex walls of MWCNTs by in situ ATRP and prepared hybrid nanostructures [190]. SWCNTs were functionalized with PS by both grafting to and grafting from methods by Qin et al. [191]. The grafting addend PS-N3 was synthesized by ATRP of styrene followed by end-group transformation and subsequent addition to SWCNT (Scheme 1.31a). The grafting from functionalization was achieved by ATRP of styrene using 2-bromopropionate groups immobilized as initiator (Scheme 1.31b) [191].

Polymer-linked MWCNT nanocomposites were prepared by reversible addition fragmentation chain transfer (RAFT). The RAFT reagent was successfully grafted on to the surface of MWCNTs and PS chains were grafted from MWCNTs via RAFT polymerization [192]. By covalently linking acyl chloride functions of functionalized MWCNTs with living polystyryllithium, Huang et al. succeeded in the preparation of polystyrene-functionalized MWCNTs (Scheme 1.32) [193].





SWCNT. The grafting from functionalization was achieved by ATRP of styrene using 2-bromopropionate groups as initiator.



**Scheme 1.32** Covalently linking of MWCNT-acyl chlorides with living polystyryllithium for the preparation of polystyrene-functionalized MWCNTs.



**Scheme 1.33** Preparation of PS by nitroxide-mediated "living" free-radical polymerization and its utilization for the functionalization of shortened SWCNTs.

Homopolymer PS and block copolymer poly(*tert*-butyl acrylate)-*b*-styrene, prepared by nitroxide-mediated "living" free-radical polymerization, were utilized for the functionalization of shortened SWCNTs through a radical coupling reaction (Scheme 1.33) [194].

#### 1.4

# Noncovalent Exohedral Functionalization - Functionalization with Biomolecules

Noncovalent functional strategies to modify the outer surface of CNTs in order to preserve the sp<sup>2</sup> network of carbon nanotubes are attractive and represent an effective alternative for sidewall functionalization. Some molecules, including small gas molecules [195], anthracene derivatives [196–198] and polymer molecules [118, 199], have been found liable to absorb to or wrap around CNTs. Nanotubes can be transferred to the aqueous phase through noncovalent functionalization of surface-active molecules such as SDS or benzylalkonium chloride for purification [200–202]. With the surfactant Triton X-100 [203], the surfaces of the CNTs were changed from hydrophobic to hydrophilic, thus allowing the hydrophilic surface of the conjugate to interact with the hydrophilic surface of biliverdin reductase to create a water-soluble complex of the immobilized enzyme [203].

The planar purple dye thionine (Fig. 1.11) was found to show strong noncovalent interactions with the sidewalls of individual CNTs. The noncovalent modification with thionine enriched the surface of the tubes with  $NH_2$  groups, opening



Fig. 1.11 Thionine and phenosafranine.

up possibilities for anchoring other molecular species such as proteins and semiconductive nanoparticles [204]. The cationic phenazine dye phenosafranine showed self-assembly to defect sites of MWCNTs. Charge-transfer complex formation was observed, associated with charge transfer from phenosafranine to electron-accepting sites of the MWCNTs [205].

Images of the assembly of surfactants on the surface of CNTs were obtained by a French group using TEM [206]. Above the critical micellar concentration, SDS formed supramolecular structures consisting of rolled-up half-cylinders on the nanotube surface (Fig. 1.12). Depending on the symmetry and the diameter of the CNTs, the formation of rings, helices and double helices was observed [206]. Similar self-assemblies have been obtained with synthetic single-chain lipids designed for the immobilization of histidine-tagged proteins. At the nanotube–water interface, permanent assemblies were produced from mixed micelles of SDS and different water-insoluble double-chain lipids after dialysis of the surfactant [206].



**Fig. 1.12** Organization of the SDS molecules on the surface of a CNT. (a) Adsorbed perpendicular to the surface, forming a monolayer; (b) organized into half-cylinders

oriented parallel to the tube axis; (c) halfcylinders oriented perpendicular to the tube axis. Copyright; reproduced with permission from *Science* International, UK [206].



**Fig. 1.13** Water-soluble SWCNTs via noncovalent sidewall functionalization with a pyrene-carrying ammonium ion.

Biological functionalization of nanomaterials has become to be of significant interest in recent years owing to the possibility of developing detector systems. Noncovalent immobilization of biomolecules on carbon nanotubes motivated the use of the tubes as potentially new types of biosensor materials [207–210] (a review on carbon nanotube based biosensors was recently published by Wang [211]). So far, only limited work has been carried out with MWCNTs [207–210]. Streptavidin was found to adsorb on MWCNTs, presumably via hydrophobic interactions between the nanotubes and hydrophobic domains of the proteins [210].

Sonication of SWCNTs in an aqueous solution of a pyrene-carrying ammonium ion (Fig. 1.13) gave a transparent dispersion/solution of the tubes. The dispersion was characterized by TEM, UV/Vis absorption, fluorescence and <sup>1</sup>H NMR spectroscopy and the results evidenced the interaction of the tube sidewalls with the pyrene moiety [212].

Simultaneous noncovalent and covalent functionalizations occur in the "intertubulary" dimers and excimers already depicted in Scheme 1.10. While the pyrene tether is covalently bound through an ester linkage with one individual SWCNT, an SWCNT dimer is formed by  $\pi$ - $\pi$  interactions of the polyaromatic pyrene system with a neighboring CNT [138].

Proteins adsorb individually, strongly and noncovalently along the nanotube lengths [213, 214]. The resulting nanotube–protein conjugates are readily characterized by AFM. Several metalloproteins and enzymes have been bound on both the sidewalls and the termini of SWCNTs [215]. Although coupling can be controlled through variation of tube oxidative preactivation chemistry, careful control experiments and observations made by AFM suggested that immobilization is physical and does not require covalent bonding [213, 214]. Two enzymes,  $\alpha$ -chymotrypsin (CT) and soybean peroxidase (SBP), were adsorbed on SWCNTs



**Fig. 1.14**. 1-Pyrenebutanoic acid succinimidyl ester irreversibly adsorbed on to the sidewall of a SWCNT via  $\pi$ -stacking. Amino groups of a protein react with the anchored

succinimidyl ester to form amide bonds for protein immobilization. Reprinted with permission from [196]. Copyright (2001) American Chemical Society.

[215]. Both enzymes underwent structural changes upon adsorption; the SBP retained up to 30 % of its native activity upon adsorption, whereas the adsorbed chymotrypsin retained only 1 % of its native activity. AFM images of the adsorbed enzymes indicated that the SBP retained its three-dimensional shape whereas CT appeared to unfold on the SWCNT surface [215]. Prolonged incubation of SWCNTs with glucose oxidase (GOx) led to the coating of the tubes with the enzyme through nonspecific adsorption on the CNT sidewalls. The surface of the CNTs was converted from hydrophobic to hydrophilic by electrochemical, thermal and plasma oxidation treatment, providing the enhanced adsorption of antibodies [216].

The very effective  $\pi$ -stacking interactions between aromatic molecules and the graphitic sidewalls of SWCNTs were demonstrated by the aggregation of the bifunctional *N*-succinimidyl-1-pyrenebutanoate [196], irreversibly adsorbed on the hydrophobic surfaces of the SWNT. With these conjugates, the succinimidyl group was nucleophilically substituted with amino groups from proteins such as ferritin or streptavidin (Fig. 1.14) and caused immobilization of the biopolymers at the tube surfaces [196].

Multilayer polymeric shells surrounding CNTs have been formed by a layer-bylayer deposition of oppositely charged polyelectrolytes [217]. The CNTs were first



**Fig. 1.15** Multilayer polymeric shells surrounding CNTs by a layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes.

functionalized by cationic 1-pyrenepropylamine, followed by a stepwise deposition of negatively charged polystyrene sulfonate (PSS) and positively charged poly(diallyldimethylammonium chloride) (PDDA) (Fig. 1.15). The formation of nanometer-thick amorphous alternating PSS and PDDA layers was confirmed by TEM images and element mapping with energy-filtered TEM [217].

The  $\pi$ -stacking of SWCNTs with polyaromatics was used by Liu et al. [218] in the self-assembling of gold nanoparticles to soluble SWCNTs. 17-(1-Pyrenyl)-13-



Fig. 1.16  $\pi$ -Stacking of 17-(1-pyrenyl)-13-oxaheptadecanethiol (PHT) with SWCNTs and self-assembling of gold nanoparticles from a colloidal gold solution.

oxaheptadecanethiol (PHT) was noncovalently attached on the nanotube surface by  $\pi$ - $\pi$  interactions and subsequently treated with a colloidal gold solution (Fig. 1.16). Self-assembling of additional gold nanoparticles resulted in a dense coverage of the nanotube surface [218].

MWCNTs were functionalized with iron phthalocyanines (FePc) to improve the sensitivity towards hydrogen peroxide. A highly sensitive glucose sensor with an FePc-MWCNT electrode based on the immobilization of GOx on poly(*o*-amino-phenol) (POAP)-electropolymerized electrode surface [219]. A hemin-modified MWCNT electrode to be used as a novel O<sub>2</sub> sensor was obtained by adsorption of hemin at MWCNTs and the electrochemical properties of the electrode were characterized by cyclic voltammetry [220].

Direct, nonsurfactant-mediated immobilization of metallothionein proteins [207–209] and streptavidin [210] at MWCNTs has also been carried out, the hydrophobic regions of the proteins probably being responsible for the adsorption. Specific affinity binding of proteins to unmodified SWCNT sidewalls was demonstrated by the adsorption of monoclonal antibodies, IgG, specific for  $C_{60}$  fullerenes, in aqueous solution. The affinity binding originated from the structural similarity of the tube sidewall graphite network and the  $C_{60}$  fullerene [221]. It was shown that the specific binding site of the IgG antibody is a domain of hydrophobic amino acids.

Recently, using electron-accepting CNTs and porphyrin derivatives as electrondonating components, a number of photoactive charge-transfer systems have been designed by Guldi and Prato, with great promise as biomimetic assemblies for photochemical energy conversion [222]. Van der Waals and electrostatic interactions served to integrate electron-accepting SWCNTs and a suitably functionalized light-harvesting polythiophene chromophore into nanostructured ITO elec-



**Fig. 1.17** Structures of SWCNT-pyrene<sup>+</sup>-ZnP<sup>8-</sup> and SWCNT-PSS<sub>n</sub><sup>-</sup>-H<sub>2</sub>P<sup>8+</sup> nanohybrids.

trodes, exhibiting photoconversion efficiencies between 1.2 and 9.3 % upon illumination [223]. Similar associative interactions represented the assembling forces in the integration of SWCNTs, negatively charged pyrene derivatives and metalloporphyrins  $MP^{8+}$  into functional nanohybrids. Upon photoexcitation, a rapid charge separation caused the reduction of the electron-accepting SWCNT and, simultaneously, the oxidation of the electron-donating  $MP^{8+}$ . The long-lived radical ion pairs exhibited lifetimes in the microsecond range, confirmed by transient absorption measurements [224]. Incorporation of SWCNT hybrids – noncovalently linked SWCNT–pyrene<sup>+</sup> and covalently linked SWCNT–PSS<sup>-</sup><sub>n</sub> – on semitransparent ITO electrodes led to suitable solar-energy conversion devices (Fig. 1.17) [225]. Novel donor–acceptor nanoassemblies have been prepared using pristine SWCNTs as electron acceptor components in "polymer wraps", with PMMA chains carrying tris(4-sulfonatophenyl)porphyrin (H<sub>2</sub>P) subunits as excited-state electron donors [226].

Dieckmann et al. in 2003 described an amphiphilic  $\alpha$ -helical peptide specifically designed to coat and solubilize CNTs and to control the assembly of the peptide-coated nanotubes into macromolecular structures through peptide–peptide interactions between adjacent peptide-wrapped nanotubes [227]. They claimed that the peptide folds into an amphiphilic  $\alpha$ -helix in the presence of carbon nanotubes and disperses them in aqueous solution by noncovalent interactions with the nanotube surface. EM and polarized Raman studies revealed that the peptide-coated nanotubes assemble into fibers with the nanotubes aligned along the fiber axis. The size and morphology of the fibers could be controlled by manipulating the solution conditions that affect peptide–peptide interactions [227].

Pronounced noncovalent interactions were found between SWCNTs and anilines [228] and also between several types of alkylamines [229]. These interactions were detected by the change in electrical conductivity of SWCNTs upon adsorption of primary amines and by their high solubility (up to 8 mg mL<sup>-1</sup>) in anilines. Presumably, as in the case of  $C_{60}$  fullerenes [230], donor–acceptor complexes are formed, as the curvature present in both materials classes lends acceptor character to the corresponding molecular carbon networks [231]. The stable aniline solutions of SWNTs can be diluted with other organic solvents without causing precipitation of the tubes.

Polymers have also been used for the formation of supramolecular complexes of CNTs. Thus, the suspension of purified MWCNTs and SWCNTs in the presence of conjugated polymers such as poly(*m*-phenylene-*co*-2,5-dioctoxy-*p*-phenylenevinylene) (PmPV) in organic solvents led to hybrid systems, the polymer wrapping around the tubes [232–234]. The properties of these supramolecular compounds were markedly different from those of the individual components. For example, the SWCNT–PmPV complex exhibited a conductivity eight times higher than that of the pure polymer, without any restriction of its luminescence properties. AFM showed that the tubes were uniformly coated by the polymer. The small average diameter of the complexes (about 7.1 nm) suggested that most of the tube bundles were broken upon complex formation. The promising optoelectronic properties of the SWCNT–PmPV complexes have been used in the manufacture of photovoltaic devices [233]. Mono- to triple-layer devices of this CNT composite have been tested as electron transport layers in organic light-emitting diodes [234].

By coating with a conjugate polymer, Murphy et al. also succeeded in developing an experimental technique for a high-yield, nondestructive purification and quantification method for MWCNTs [235]. The polymer host selectively suspends nanotubes relative to impurities and, after removal by filtration, a 91 % pure CNT fraction was obtained [235]. The wrapping of SWNTs with polymers carrying polar side-chains such as polyvinylpyrrolidone (PVP) or PSS led to stable solutions of the corresponding SWCNT–polymer complexes in water [236], the SWCNT– PVP complex exhibiting liquid crystalline properties. The thermodynamic driving force for this complex formation is suggested to be the avoidance of unfavorable interactions between the apolar tube walls and the solvent water.

The wrapping of polymer ropes around MWCNTs occurs in a well-ordered periodic fashion [237]. The authors suggested that the polymer intercalated between the nanotubes, leading to unraveling of ropes and causing a decrease in interactions between the individual CNTs. Moreover, Raman and absorption studies suggested that the polymer interacts preferentially with CNTs of specific diameters or a specific range of diameters [238].

A molecular dynamics simulation in conjunction with experimental evidence was used to elucidate the nature of the interactions between polymer materials and CNTs [239]. Computational time was reduced by representing CNTs as a force field. The calculations indicated an extremely strong noncovalent binding energy. Furthermore, the correlation between the chirality of the nanotubes and mapping of the polymer on to the lattice was discussed [239].

Grafting shortened SWCNTs with PEG by microwave-assisted heating allowed for soluble derivatives of SWCNTs, and remarkably enhanced reaction rates were observed compared with conventional heating [240].

Sidewalls of CNTs were coated with PEG [241], preventing the nonspecific adsorption of proteins [242, 243]. The polymeric layer was subsequently used as an interface for the specific coupling or affinity binding of proteins [242]. By a diamine-terminated oligomeric PEG functionalization, the solubilization of as-prepared and purified SWCNTs was achieved [244]. The soluble tubes were characterized by spectroscopic, microscopic and gravimetric techniques.

A nonwrapping approach to noncovalent engineering of CNT surfaces by short and rigid conjugated polyarylenethynylenes was reported [199]. This technique allowed for the dissolution of various types of CNTs in organic solvents and the introduction of numerous neutral and ionic functionalities onto the CNT surfaces [199].

A family of poly[(*m*-phenylenevinylene)-*co*-(*p*-phenylenevinylene)]s (PamPV), functionalized in the synthetically accessible C-5 position of the *meta*-disubstituted phenylene rings, have been designed and synthesized [245]. They have been prepared both (1) by the polymerization of *O*-substituted 5-hydroxyisophthalaldehydes and (2) by chemical modifications carried out on polymers bearing reactive groups at the C-5 positions. PAmPV polymers solubilize SWNT bundles in organic solvents by wrapping themselves around the nanotube bundles. Specifically functionalized PAmPV derivatives wrapped around SWCNTs can form pseudorotaxanes along the walls of the CNTs in a periodic fashion. The formation of such polypseudorotaxanes has been investigated in solution by NMR and UV/Vis spectroscopy, and also on SiO<sub>2</sub> wafers in the presence of SWCNTs by AFM and surface potential microscopy [207].

The solubilization of oxidized carbon nanotubes has been achieved through derivatization using an amino-functionalized crown ether (Scheme 1.34). According to optical measurements, the resultant adduct allowed concentrations of dissolved CNTs of the order of 1 g L<sup>-1</sup> in water and in methanol [246]. The CNT–crown ether adduct was readily redissolved in different organic solvents at substantially high concentrations. Characterization of the solubilized adducts was performed with <sup>1</sup>H NMR spectroscopy; <sup>7</sup>Li NMR spectroscopy was used to examine the ability of the crown ether macrocycle to bind Li<sup>+</sup> ions. Furthermore, the solutions were analyzed using UV/Vis spectroscopy, photoluminescence and FT-IR spectroscopy and were structurally characterized by AFM and TEM. The adduct formation likely resulted from noncovalent chemical interactions between the carboxylic groups of the oxidized tubes and amine moieties attached to the crown ethers [246].



Scheme 1.34 Derivatization of SWCNTs with an amino-functionalized crown ether.



**Fig. 1.18** Schematic illustration of (a) a globular protein, adsorbed on (b) a nanotube and (c) an AFM image, showing protein (bright dot-like structures decorating the line-

like nanotube) nonspecifically adsorbed on a nanotube. Reprinted with the permission of the National Academy of Sciences of the USA [247].

SWCNTs were exploited as a platform to investigate surface–protein and protein–protein binding and to develop specific electronic biomolecular detectors [247]. The nonspecific binding on nanotubes (Fig. 1.18) was overcome by immobilization of poly(ethylene oxide) (PEO) chains. A general approach was then advanced to permit the selective recognition and binding of target proteins by conjugation of their specific receptors to PEO-functionalized nanotubes. This scheme, combined with the sensitivity of nanotube electronic devices, enables highly specific electronic sensors to be obtained for detecting clinically important biomolecules such as antibodies associated with human autoimmune diseases [247].

Prakash et al. [248] visualized individual CNTs by fluorescence microscopy through noncovalent labeling with conventional fluorophores (Fig. 1.19). Reversal of contrast in fluorescence imaging of the CNTs was observed when the labeling procedure was performed in a nonpolar solvent. The results were consistent with a CNT–fluorophore affinity mediated by hydrophobic interaction, the reverse-contrast images also provided a clear indication of the nanotube location [248].

Norbornene polymerization was initiated selectively on the surface of SWCNTs via a specifically adsorbed pyrene-linked ring-opening metathesis polymerization initiator (Fig. 1.20). The adsorption of the organic precursor was followed by cross-metathesis with a ruthenium alkylidene, resulting in a homogeneous non-covalent poly(norbornene) (PNBE) coating [249].



Fig. 1.19 Chemical structures of conventional fluorophores used for noncovalent labeling of individual CNTs for fluorescence microscopy.



**Fig. 1.20** Functionalization strategy for a polynorbornene (PNBE) coating of SWCNTs. Path A: adsorption of organic precursors (a)

or (b) followed by cross-metathesis with a ruthenium alkylidene. Path B: adsorption of a pyrene-substituted ruthenium alkylidene (c).

Oligonucleotides and DNA molecules were nonspecifically bound to MWCNT sidewalls via nonspecific interactions and visualized by HR-TEM [208, 209]. Certain organizational properties of CNT–DNA systems have been reported [208, 250]. Nonspecific interactions of oligonucleotides with CNTs enhanced the polymerase chain reaction (PCR), due to the local increase in the reaction components on the surface of the CNTs [251]. HiPCO SWCNTs were dispersed into aqueous double-stranded DNA solutions forming stable solutions. With semiconducting DNA-wrapped HiPCO tubes, the first optical interband transitions of the wrapped tubes displayed a unique pH dependence [252]. When single-stranded DNA was used as dispersing agent and SWCNTs were dispersed, AFM investigations from this suspension showed isolation of the tubes from the pristine bundles and the removal of contaminating particles. Consequently, this biofunctionalization technique also represents a purification method for SWCNTs [253].

### 1.5

### **Endohedral Functionalization**

Endohedral functionalization of CNTs is the filling of the tubes with various atoms or small molecules [254]. The internal cavity of CNTs (1–2 nm in diameter) provides space for the accommodation of guest molecules [254–260]. Even small proteins and other biomolecules [207, 208, 261] and oligonucleotides [262] have been trapped in the nanotube cavity. In 1998, Luzzi's group [263] for the first



Fig. 1.21  $C_{60}$ @SWCNT: computer simulation, rendered armchair SWCNT filled with  $C_{60}$  fullerenes.

time observed the formation of single-walled carbon nanotubes containing  $C_{60}$  fullerenes by means of HR-TEM and the term "fullerene peapods" was created for  $(C_{60})_n @SWCNTs$  (Fig. 1.21). The incorporation of fullerenes such as  $C_{60}$  [264, 265] or the metallofullerene Sm@C<sub>82</sub> [266] is an impressive example of the endohedral chemistry of SWCNTs [254].



**Fig. 1.22** (A) HR-TEM micrograph of an isolated SWCNT containing  $Gd@C_{82}$  (scale bar = 5 nm); (B) Schematic presentation of  $(Gd@C_{82})_n@SWCNT$  (distance between the

metallofullerenes  $a \approx 1.10$  nm; intertube distance in the bundles  $b \approx 1.89$  nm). Reprinted with permission of the American Physical Society [267].

The incorporation of guest molecules can be achieved during their growth or is executed at defect sites and holes via wet chemistry, by surface diffusion and gasphase transport. Encapsulated fullerenes tend to form chains that are coupled by van der Waals forces. Upon annealing, the encapsulated fullerenes coalesce in the interior of the SWCNTs, resulting in pill-shaped, concentric, endohedral capsules a few nanometers in length [265]. The progress of such reactions inside the tubes could be monitored in real time by use of HR-TEM [266].

In the class of metallofullerene peapods, in addition to  $Gd@C_{82}$ -containing peapods (Fig. 1.22) [267], also  $Dy@C_{82}$ -,  $La@C_{82}$ - and  $Sm@C_{82}$ -containing peapods and dimetallofullerene-containing peapods with peas of the kind of  $Ti_2@C_{80}$ ,  $La_2@C_{80}$  and  $Gd_2@C_{92}$  have been synthesized (see the references in [254]).

In addition to doping with fullerenes, SWCNTs can also be filled with molecules such as ferrocene, chromocene, ruthenocene, vanadocene and tungstenocene dihydride. The filling with metallocenes occurred from the vapor phase with formation of collinear metallocene chains inside the nanotubes [268]. Also the filling with Zn diphenylporphyrin was successful and established from absorption spectra and Raman measurements [269].

# 1.6 Conclusions

These examples of functionalization of carbon nanotubes demonstrate that the chemistry of this new class of molecules represents a promising field within nanochemistry. Functionalization provides for the potential for the manipulation of their unique properties, which can be tuned and coupled with those of other classes of materials. The surface chemistry of SWCNTs allows for dispersibility, purification, solubilization, biocompatibility and separation of these nanostructures. Additionally, derivatization allows for site-selective nanochemistry applications such as self-assembly, shows potential as catalytic supports, biological transport vesicles, demonstrates novel charge-transfer properties and allows the construction of functional nanoarchitectures, nanocomposites and nanocircuits.

# 1.7

# Experimental

In the following, the experimental details of different functionalization techniques are presented. Although the selection of the examples is rather arbitrary, an attempt has been made to give a general overview of the manifold methodologies of functionalization, each experimental description standing for a representative example of an individual functionalization method.

# Fluorination of CNTs – synthesis of F-SWCNTs

Amounts of 1.5–10 mg of highly purified laser-ablated SWCNTs in the form of a bucky paper were placed in a temperature-controlled fluorination reactor. After purging in He at 250 °C, elemental fluorine, purified from HF by passing it over NaF pellets (HF trap), was introduced. The fluorine flow was gradually increased to a flow-rate of 2 sccm diluted in an He flow of 20 sccm. The fluorination was allowed to proceed for ~10 h, at which point the reactor was brought to room temperature and the fluorine flow was gradually lowered. When the fluorine flow had completely halted, the reactor was purged at room temperature for ~30 min before removing the fluorinated products. The F-SWCNTs consisted of approximately 30 at. % fluorine, determined by electron microprobe analysis (EMPA) [29].

# Oxidative purification - carboxylation of SWCNTs

A 1.100-mg amount of SWCNT raw material was heated under reflux in 150 mL of 65 % HNO<sub>3</sub> for 3 h. Subsequently, the black solution was centrifuged and a black sediment remained at the bottom of the centrifuge jar. The clear, brownish yellow supernatant acid solution was decanted off. The sediment was treated by repeated resuspension in distilled water, followed by centrifugation and decantation of each of the supernatants. The remaining sediment was dispersed in distilled water and treated with two or three short (0.5 s) ultrasonic pulses. For permanent storage the solution was brought to pH 8–9 using potassium carbonate [53].

# Amidation - formation of CNT-carboxamides

For an octadecylamide derivatization, 100 mg of dried, cut SWCNTs, 270 mg ODA and 210 mg of DCC were added to dry DMF and stirred under Ar for 24 h. After the reaction, the reaction mixture was filtered off over 0.2-µm pore size membrane filters, washed with ethanol and acetone and dried in vacuum for 12 h. The thus derivatized ODA-SWCNTs turned out to be fairly soluble in ODCB ( $\sim 1$  mg mL<sup>-1</sup>), the suspensions were stable over at least several months under ambient conditions and an estimated 4 % of the SWCNT carbons were functionalized [99].

# Addition of nucleophilic carbenes - imidazolidene-SWCNTs

A 200-fold excess of freshly prepared and filtered (Celite) solution of the nucleophilic carbene dipyridylimidazolidene was added to a dispersion of SWCNTs in THF at -60 °C. After stirring at -60 °C for 3 h, the reaction mixture was slowly warmed to room temperature and then diluted with ethanol. The precipitated functionalized nanotubes were isolated by centrifugation and washed with ethanol [148].

### Addition of nitrenes - ethoxycarbonylaziridino-SWCNTs

Purified SWCNTs are dispersed in 1,1,2,2-tetrachloroethane (TCE) in an ultrasonic bath under a nitrogen atmosphere over several hours. The suspension is heated to 160 °C and a 200-fold excess of ethyl azidoformate as nitrene precursor

is added dropwise. After thermally induced  $N_2$  extrusion, nitrene addition results in the formation of ethoxycarbonylaziridino-SWCNTs which precipitate after a short time. Work-up proceeds by centrifugation and washing of the insoluble residue with diethyl ether [148, 154].

# Functionalization via the Bingel reaction

A 1.10-mg amount of purified SWCNT material was annealed under vacuum  $(10^{-3} \text{ mbar})$  at 1000 °C for 3 h prior to use. To a suspension of this material in dry ODCB, 1.8 mmol of diethyl bromomalonate and 3.3 mmol of DBU were added. The mixture was allowed to react for 2 h under stirring. The modified SWCNTs were isolated from the reaction mixture by filtration and washed thoroughly with ODCB followed by ethanol [160].

### Azomethine ylides - functionalization with amino acids

N-(N-Boc-8-amino-3,6-dioxaoctylglycine and paraformaldehyde were added to a suspension of CNTs in DMF and the mixture was heated at 130 °C for 96 h. After separation of unreacted material by filtration and subsequent evaporation of the solvent, the residue was diluted with chloroform and washed with water. The organic phase was dried and the solvent was evaporated. The N-Boc-aminotriethylene glycol-functionalized CNTs were isolated by precipitation with diethyl ether and filtration, and the filter cake was subsequently washed several times with diethyl ether. To a solution of such functionalized CNTs in DCM, gaseous HCl was bubbled through to remove the protecting group (Boc) at the chain end. The CNT ammonium chloride salt precipitated during the acid treatment. After removal of the solvent, the brown solid was dissolved in methanol and precipitated with diethyl ether. To derivatize these SWCNTs with N-protected glycine, Fmoc-Gly-OH was activated with N-hydroxybenzotriazole (HOBT) and diisopropylcarbodiimide (DIC) in DMF-DCM for 15 min and added to a suspension of the in DCM, previously neutralized with diisopropylethylamine (DIEA). After stirring at room temperature for 2 h, the coupling reaction was terminated and the solvent was completely evaporated. The raw material was dissolved in DCM and the derivatized SWCNTs were reprecipitated several times by addition of diethyl ether [170].

### Functionalization by Diels-Alder cycloaddition

An amount of 1.20 mg (0.9 mmol) of pentyl carboxylate-functionalized SWCNTs (Scheme 1.23) was mixed with 150 mg (0.9 mmol) of 4,5-benzo-1,2-oxathiin-2-oxide in 40 mL of ODCB and the mixture was irradiated in a focused microwave reactor at 150 W for 45 min. The ODCB was removed by vacuum distillation and the residue was purified by washing several times with pentane and diethyl ether to obtain benzobutenylene-functionalized SWCNT as a dark-brown solid [171].

# Functionalization with in situ-generated diazonium compounds

About 8 mg of HiPCO SWCNTs, purified by oxidation in wet air at 250 °C, were sonicated for 10 min in 10 mL of ODCB. To this suspension was added a solution of the aniline derivative (2.6 mmol,  $\sim$  4 equiv. per mole of carbon) in 5 mL of acetonitrile. After transfer to a septum-capped reaction tube and bubbling with nitrogen for 10 min, 4.0 mmol of isoamyl nitrite were quickly added. The septum was removed and replaced with a Teflon screw-cap and the suspension was stirred at 60 °C for 15 h. (CAUTION! Considerable pressure was generated in the vessel due to the nitrogen evolved. This was alleviated by partially unscrewing the cap for venting every 30 min for the first 3 h). After cooling to 45 °C, the suspension was diluted with 30 mL of DMF, filtered over a PTFE (0.45  $\mu$ m) membrane and washed extensively with DMF. Repeated sonication in and washing with DMF were used for purification of the material [176a].

Electrochemical functionalization – reductive coupling of diazonium salts The electrochemical functionalization of SWCNTs, deposited on an Si/SiO<sub>2</sub> substrate, with 4-nitrophenyl groups succeeded by the reduction of 4-nitrobenzenediazonium salt in a mini-electrochemical cell with platinum counter and (pseudo-)reference electrodes. A probe needle was used to make contact with one of the Au–Pd bonding pads on the substrate and allowed the application of an electric potential to the electrode (–1.3 V vs. Pt for >30 s) and to any SWCNTs underneath the electrode [177b].

### Reductive alkylation - synthesis of 2-[2-(2-methoxyethoxy)ethyl]-MWCNTs

Into a dry and nitrogen-purged three-necked flask, equipped with a gas inlet and a condenser, 500 mL of anhydrous ammonia were condensed at -70 °C; 2 g (87 mmol) of sodium were added and a dark-blue solution was formed. To this mixture, 50 mg (4.2 mmol of carbon) of MWCNTs were added and a black solution of the tubes was obtained. Stirring was continued for 1 h. Subsequently, 1.63 mL (12 mmol) of 1-bromo-2-(2-methoxyethoxy)ethane was added dropwise and the reaction mixture was stirred overnight to remove the ammonia slowly. Water (100 mL) was carefully added to the black solid. After acidification with 20 mL of dilute (10%) HCl, the nanotubes were extracted with 200 mL of hexane and washed with water. The organic phase was filtered through a 200-nm PTFE membrane filter and washed with ethanol and THF. The resulting black solid was dried in a vacuum oven at 50 °C overnight [270].

Addition of carbanions – syntheses of *tert*-butyl-H-SWCNTs and of *tert*-butyl-SWCNTs In a nitrogen-purged flask, equipped with a gas inlet and a pressure compensator, 20 mg of HiPCO tubes (1.7 mmol of carbon) was dispersed in 50 mL of anhydrous benzene. To this dispersion 2.5 mL of a 1.7 M solution of *tert*-butyllithium (4.25 mmol) in hexane were added dropwise over a period of 10 min. Subsequently, the suspension was additionally stirred for 1 h at room temperature and the SWCNT dispersion turned into a black homogeneous solution. The solution was stirred for a further 1 h and subsequently quenched by the addition of

dilute HCl. The resulting dispersion was diluted with 100 mL of acetone and filtered through a 0.2-µm PTFE membrane filter and washed with ethanol and THF. The resulting black solid was dried in vacuum at 50 °C overnight [270]. Instead of quenching the negatively charged intermediates *tert*-butyl-SWCNTs to yield the reduced *tert*-butyl-H-SWCNTs, the intermediates could subsequently be reoxidized by bubbling oxygen through the homogeneous black dispersion. Thus, *tert*-butyl-SWCNTs were formed, and the workup was achieved by addition of cyclohexane, purging with water and diluted HCl, membrane filtration, washing with THF, MeOH and EtOH, and drying under vacuum at 50 °C [271].

Covalent functionalization by polymerization – polystyrene grafted to SWCNTs Nitroxide-terminated PS samples were prepared by "living" free-radical polymerization utilizing an alkoxyamine unimolecular initiator. A 10-mg amount of purified and shortened sWCNTs was dispersed in anhydrous DMF and 500 mg of nitroxide-terminated PS along with a catalytic amount of acetic anhydride (50  $\mu$ L) were added. After bubbling with N<sub>2</sub> for 30 min, the mixture was immersed in a 125 °C oil-bath and stirred under Ar for 3 days. Upon cooling, the reaction mixture was filtered through a 200-nm pore-diameter PTFE membrane and washed with THF and DCM (200 mL each) to remove unreacted PS. The residual black solid was peeled away from the membrane and dried at 50 °C under vacuum overnight [194].

 $\pi$ -Stacking of 1-pyrenebutanoic acid succinimidyl ester on SWCNT sidewalls SWCNTs were suspended on meshed gold grids according to known methods and a grid sample was incubated in a 1-pyrenebutanoic acid succinimidyl ester solution (6 mM in DMF or 1 mM in methanol) for 1 h at room temperature, after which the sample was rinsed three times in pure DMF or methanol [196].

Noncovalent functionalization - incubation with surfactants and lipids

A 1-mL aqueous solution of SDS [1% by weight, concentration greater than the critical micellar concentration (CMC)], was sonicated with 1 mg of SWCNTs or MWCNTs. Similarly, an aqueous solution (1 mg mL<sup>-1</sup>) of an amphiphilic monochain lipid reagent, e.g. an octadecanoyl moiety linked with nitrilotriacetic acid, was sonicated with 1 mg of MWCNTs for 3 min [206].

Endohedral functionalization – encapsulating metallofullerenes –  $(Gd@C_{82})_n@SWCNTs$ 

Gd@C<sub>82</sub> was generated by arc discharge using a Gd–graphite rod and isolated by a multistage HPLC technique; SWCNT bundles were prepared by pulsed-laser evaporation. The doping of Gd@C<sub>82</sub> into the inner hollow space of SWCNTs was carried out in a sealed glass ampoule at 500 °C for 24 h. Prior to the introduction of SWCNTs to the ampoule, the SWCNTs were heated in dry air at 420 °C for 20 min [267].

## List of Abbreviations

AFM	atomic force microscopy	PMMA	poly(methyl methacrylate)
ATRP	atom transfer radical	PS	polystyrene
	polymerization	PSS	polystyrene sulfonate
CNT	carbon nanotube	PTC	phase-transfer catalysis
CVD	chemical vapor deposition	PVP	polyvinylpyrrolidone
DBU	1,8-diazabicyclo[5.4.0]	RBM	Raman breathing mode
	undecene	SCW	supercritical water
DCC	dicyclohexylcarbodiimide	SDS	sodium dodecyl sulfate
DCM	dichloromethane	SEM	scanning electron
DMF	dimethylformamide		microscopy
DOS	density of states	STM	scanning tunneling
DPI	dipyridylimidazolidene		microscopy
GCE	glassy carbon electrode	SWCNT	single-walled carbon
HiPCO	high pressure		nanotube
	CO conversion	TEM	transmission electron
MMA	methyl methacrylate		microscopy
MWCNT	multiwalled carbon	TGA	thermogravimetric analysis
	nanotube	THF	tetrahydrofuran
ODA	octadecylamine	XPS	X-ray photoemission
			spectroscopy

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