

Current Progress on the Chemical Modification of Carbon Nanotubes

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Nikolaos Karousis received his B.Sc. Degree in Chemistry in 1995 and his Ph.D. Degree in Organic Chemistry in 2003, at the University of Ioannina, Greece. During the years 2004 and 2005, he was a postdoctoral fellow on a research project financially supported from the Greek General Secretariat of Research and Technology (GSRT). In 2006, he joined the Dr. N. Tagmatarchis group at the Theoretical and Physical Chemistry Institute (TPCI) in the National Hellenic Research Foundation (NHRF), and was introduced in the chemistry of carbon nanostructured materials. His current research interests lie in the chemical modification of carbon nanotubes, carbon nanohorns, and graphene-based materials, for nanotechnological applications. He has published more than 10 papers in refereed scientific journals and made over 10 announcements at international scientific conferences.

considered as rolled-up graphene sheets, the ends of which are capped with a hemisphere of a buckyball structure. The exact structure of a nanotube depends on the different angles and curvatures in which a graphene sheet can be rolled into a tube and is determined by a single vector, which is called a chiral vector and discriminates CNTs into “zigzag”, “armchair”, and “chiral” forms. The electronic properties of a nanotube change in correspondence to its structure; thus armchair nanotubes are metallic, while zigzag and chiral can be either metallic or semiconducting. In general, single-walled carbon nanotubes (SWCNTs) are a mixture of metallic and semiconducting material, depending sensitively on their geometrical features, while multiwalled carbon nanotubes (MWCNTs) are regarded as metallic conductors. Especially for SWCNTs, the electronic properties vary from metallic to semiconducting depending on their structures. Additionally, as a result of the 1-D nature of CNTs, electrons can be conducted in nanotubes without being scattered. The absence of scattering of the electrons during conduction is known as ballistic transport and allows the nanotube to conduct without dissipating energy as heat.

1. Introduction

The unique morphology and structure of carbon nanotubes (CNTs) keep attracting a great number of researchers to explore the novel properties of these materials. CNTs are

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Dimitrios Tasis was born in Ioannina, Greece. He received his B.S. and Ph.D. degrees in Chemistry from the University of Ioannina in 1993 and 2001, respectively. In 2002, he moved to the laboratory of Prof. M. Prato at the University of Trieste, Italy, for two years as a postdoctoral fellow, working with carbon nanotubes and fullerenes. Since early 2004, he has been teaching in the department of Materials Science at the University of Patras, Greece, currently as an assistant professor (under contract). His research interests lie in the chemistry of carbon-based nanostructures such as carbon nanotubes and graphene as well as their polymer composites for advanced mechanical/electrical properties. He has published more than 25 research articles in peer-reviewed journals and has been invited to many international conferences.

However, as prepared CNTs possess a variety of diameters, length distribution, and structures within the same sample. It is also well-known that the methods of production of CNTs generate impurities such as byproduct carbonaceous species

and residues from the transition metal catalysts used in preparing CNTs. Moreover, CNTs are insoluble in all solvents due to strong van der Waals interactions that tightly hold them together, forming bundles. All of the above decrease the overall yield of usable material and interfere with most of the desired properties of the CNTs.

In this frame, CNTs can undergo chemical functionalization to enhance solubility in various solvents and to produce novel hybrid materials potentially suitable for applications (Figure 1). The main approaches for the functionalization of CNTs can be grouped into two main categories: (a) the covalent attachment of chemical groups, through reactions on the conjugated skeleton of CNTs, and (b) the noncovalent supramolecular adsorption or wrapping of various functional molecules onto the tubes. The covalent functionalization of CNTs allows functional groups to be attached to tube ends or sidewalls. The sites of highest chemical reactivity in the CNT structure are the caps, which have a semifullerene-like structure. Chemical functionalization of CNT tips has been performed mainly on the basis of oxidative treatments. As a general rule, CNT oxidation yields opened tubes with oxygen-containing functional groups (predominantly carboxylic acid) at both the sidewall and the tube endings. These groups can then be used as chemical anchors for further derivatization. Although the bonding in CNTs is similar to that of graphene, curvature of the nanotube sidewall renders addition reactions to the cylindrical nanostructure more favorable than in a flat graphene sheet.¹ In addition, several experimental studies exist, which reveal that the exohedral chemical reactivity increases with increasing curvature of the sidewall. This dependency has been attributed to curvature-induced strain that originates from pyramidalization of the sp^2 -hybridized carbon atoms and the misalignment of π -orbitals.²

Another parameter that profoundly alters the chemical reactivity of CNT sidewalls is the presence of defects. It has been estimated that approximately 2% of the carbon atoms in SWCNTs occur in nonhexagonal rings. The presence of sidewall defects such as vacancies or pentagon–heptagon pairs (Stone–Wales defects) results in a locally enhanced chemical reactivity of the graphitic nanostructures. Apparently, covalent sidewall functionalization generates sp^3 carbon sites on CNTs, which disrupt the band-to-band transitions of π electrons, and cause loss of the novel properties of CNTs, such as their high conductivity and remarkable mechanical properties. With increasing functionalization degree, the tubes can eventually convert into insulating material. Partial restoring of the structural integrity of the starting material can be accomplished by thermal annealing of the modified tubes at temperatures between 300 and 500 °C.

On the other hand, a different approach to exfoliate the CNTs bundles is the noncovalent functionalization. In this frame, the tube surface can be modified via van der Waals forces and π – π interactions, by adsorption or wrapping of polynuclear aromatic compounds, surfactants, polymers, or biomolecules. The main advantage of the noncovalent functionalization of CNTs, as compared to the covalent one, is that with the former, chemical functionalities can be introduced to the CNTs without affecting the structure and electronic network of the tubes.

Previously, we reviewed the field of CNT chemical functionalization, gathering examples from the literature from the very first report on the solubilization of CNTs, a decade

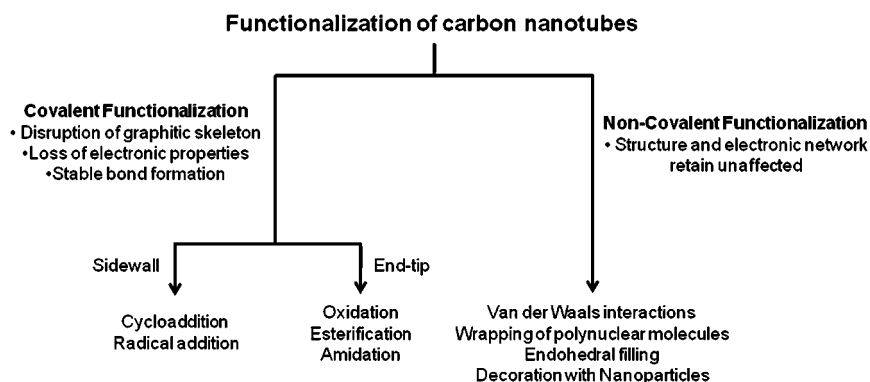


Figure 1. Overview scheme of the functionalization of carbon nanotubes.

back in time, up to the first half of the year of 2005.³ Given the continuous growth in the field, as highlighted from the high number of reports in the literature as well as the plethora of citations received, we felt it appropriate to expand and update, in a new review article, the progress in the area. In the current Review, which is a continuation of the previous one complementary to other review articles recently appearing in the literature,⁴ important and intriguing results on the functionalization and solubilization of CNTs, from the second half of 2005 up to date, are presented and critically analyzed. The organization of this Review is as follows: the first section is dedicated to the covalent functionalization of CNTs, in the second section the noncovalent modification of CNTs is surveyed, and finally the last section contains some concluding remarks. It should be mentioned here that the drawings shown are only graphic illustrations, in which an arm-chair SWCNT-model template is chosen, screening the several different ways of functionalization of CNTs, and do not represent the precise type of CNTs used in each case, or the exact position and the degree of functionalization.

2. Covalent Approaches

2.1. Defect Site Chemistry — Oxidation Reactions

Among various surface functionalization techniques, oxidation of CNTs is probably the most widely studied. Early treatment techniques involved gas-phase oxidation in air and oxidative plasmas. Only recently, a gas-phase route, involving treatment with nitric acid vapor, proved to be efficient enough for the introduction of oxygen species on the sidewalls of CNTs, simplifying the oxidation procedure by avoiding filtration, washing, and drying steps.⁵ Liquid-phase oxidation mainly involved acidic etching by hot nitric acid or sulfuric/nitric acid mixtures.⁶ Recent studies suggested the loss of SWCNT metallic character^{7a} and the differentiation of the influence of physical properties for different types of MWCNTs^{7b} via nitric acid purification and functionalization, while the overoxidation of CNTs by nitric acid, followed by washing with sodium hydroxide, led to exfoliated carbonaceous fragments.^{7c} To promote acidic etching and increase the population density of surface oxide groups onto MWCNT sidewalls, Xing et al.⁸ reported the sonication-assisted oxidation of CNT material in a sulfuric/nitric acid mixture. During that procedure, some carbonyl groups were formed along with carboxy groups, with the latter taking up the greater population. Depending on the time of sonochemical treatment, relative structural damage of the surface of MWCNTs was observed, affecting their electronic properties. An evaluation of five different mild sonochemical acid

oxidation reactions for CNTs also proposed the sonication of CNTs in nitric acid followed by subsequent treatment with hydrogen peroxide as the most efficient method for the oxidation of MWCNTs without damaging their skeleton.⁹ The effect of treating MWCNTs with dilute nitric acid under supercritical water conditions was also explored.¹⁰ It was found that, as the nitric acid concentration and the reaction time were increasing, the sidewall functionalization with methylene, hydroxyl, and ether groups proceeded from the outer to the inner graphitic layers of MWCNTs.

The oxidation reaction of piranha ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) solutions onto SWCNTs was reported by Ziegler et al.¹¹ At high temperatures, treatment of CNTs with the oxidizing solution was found to attack existing defect sites, generating vacancies in the graphitic sidewalls and consuming the oxidized vacancies to yield short, cut nanotubes. Prolonged reaction time resulted in increasingly shorter nanotubes as well as selective etching of the smaller diameter nanotubes. On the other hand, room temperature piranha treatments showed the capability of cutting existing damage sites with minimal carbon loss, slow etch rates, and little sidewall damage.

Selective oxidation of SWCNTs by hydrogen peroxide was conducted at varying heating times and monitored by ultraviolet–visible–near-infrared spectroscopy.¹² A major increase in the relative absorption intensity indicated a higher than 80% content of metallic SWCNTs in the final product. Semiconducting SWCNTs were found to be more reactive than metallic ones because of the hole-doping effect by hydrogen peroxide, resulting in faster oxidation. Recently, the controlled shortening and uncapping of DWCNTs and very thin MWCNTs was achieved by using mild oxidizing agent (H_2O_2 15% solution) and reaction conditions (100 °C for 3 h).¹³ Moreover, chlorine oxoanions with different oxidation states were incubated with SWCNT material to determine how the electronic structures of the CNTs can be engineered systematically by oxidative substances.¹⁴ Raman spectroscopy showed that metallic SWCNTs were selectively suppressed by using oxidants at a high oxidation state, whereas there was a minimal effect on the semiconducting ones. Chen and co-workers¹⁵ have reported a harsh two-step process for the effective and scalable shortening (length <60 nm) and carboxylation of SWCNTs. This methodology consists of dispersing SWCNTs in oleum (100% H_2SO_4 with 3% SO_3), followed by the introduction of nitric acid as the cutting agent, into the acid-intercalated SWCNT dispersion. Oleum was effectively intercalated between individual SWCNTs, thus enhancing the efficiency of nitric acid into them. The solubility of these ultrashort carboxylated SWCNTs in organic solvents, superacid, and water was estimated to

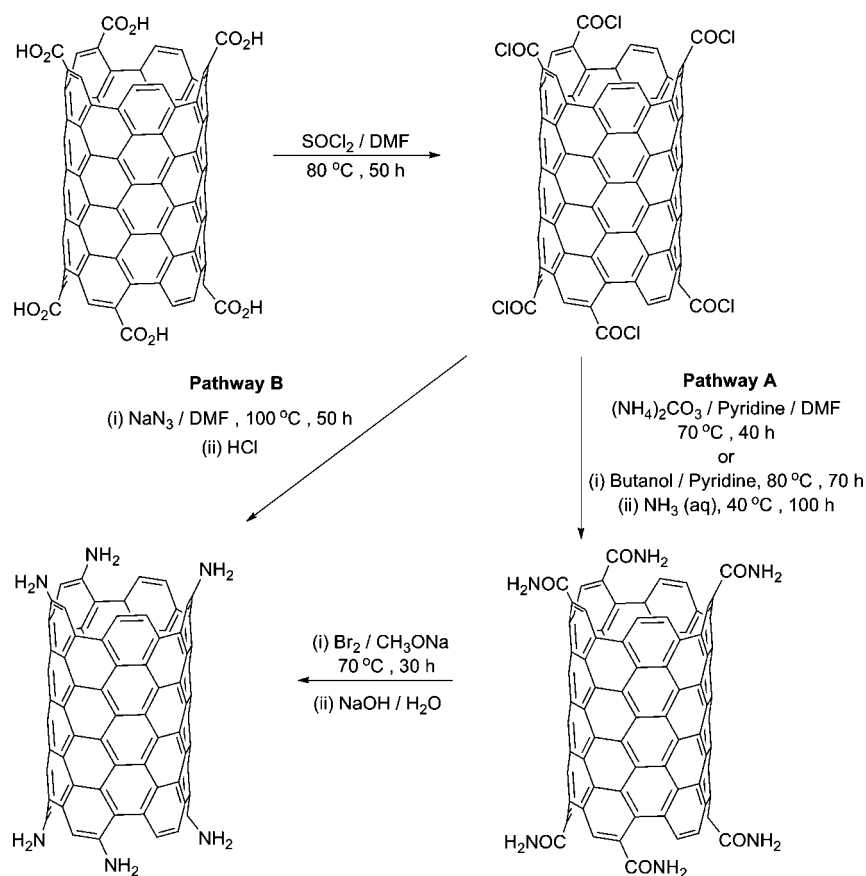


Figure 2. Preparation of amino-functionalized SWCNTs via Hofmann rearrangement of carboxylic acid amide (pathway A) and via Curtius reaction of carboxylic acid chloride with sodium azide (pathway B).

be about 2 wt %. Furthermore, Arrais and co-workers¹⁶ reported the synthesis of pH-dependent, water-dispersible, oxidized SWCNTs. By this procedure, SWCNTs were suspended in tetrahydrofuran (THF) and stirred under anaerobic conditions in the presence of a liquid metal alkali-alloy, and then subsequently the mixture was stirred under full aerobic atmosphere. The achieved products displayed an interesting pH-dependent behavior, being therein easily suspended in basic aqueous media and quantitatively precipitated under acidic conditions. In another work, the hydrophobic surface of MWCNT material was converted to hydrophilic, through exposure of tubes to UV light within an ozone chamber, followed by reduction of carboxyl groups by lithium aluminum hydride and silanization.¹⁷ The latter was achieved by using 3-glycidoxypropyltrimethoxysilane, thus resulting in the attachment of silane molecules containing epoxy end groups on the MWCNT surface.

The direct attachment of amino groups to SWCNT opened edges was reported by Gromov and co-workers.¹⁸ Two approaches were utilized for the synthesis of amino-derived SWCNTs from carboxylated SWCNTs. The first one was based on Hofmann rearrangement of the corresponding amides and the second one on Curtius rearrangement of carboxylic acid azide, followed by hydrolysis (Figure 2).

It is known that, in most cases, chemistry under microwave radiation is faster and more efficient than that under conventional chemical processing conditions.¹⁹ Moreover, microwave processing reduces the need for solvents, thus being considered environmentally friendly. Recently, microwave chemistry was also introduced to the chemistry of CNTs with very interesting results. Mitra et al.²⁰ managed to introduce carboxylic and sulfonated groups on the side-

walls of SWCNTs after microwave treatment of SWCNT material in a mixture of nitric and sulfuric acid for a time period of about 3 min. The modified tubes showed a great dispersibility in deionized water and ethanol. Elemental analysis indicated that one in three carbons on the SWCNT graphitic sidewalls were carboxylated, whereas one in 10 carbon atoms were sulfonated. Some reduction in the average length of the nanotubes as well as an enhanced disorder in the sidewalls was also observed due to functionalization. Electrical conductivity measurements of a membrane of functionalized SWCNTs showed 33% reduction as compared to the starting material, but the starting conductivity was fully recovered after high-temperature annealing under argon atmosphere.

2.2. Esterification—Amidation Reactions to Oxidized CNTs

Carboxylated CNTs were extensively used as precursors for further covalent modification of CNTs, through esterification and/or amidation reactions. In most cases, carboxylic groups that bear on the sidewalls and tips of CNTs are converted to acyl chloride groups via reaction with thionyl or oxalyl chloride, followed by the addition of the appropriate alcohol or amine. A great number of substituents, including several organic substances, biomolecules, polymers, or photosensitive compounds, were interacted with CNTs by this procedure.²¹ In particular, acyl chloride-modified MWCNTs reacted with highly branched molecules that have hydroxyl groups, like poly(benzylether)²² and poly(amidoamine) (PAMAM) dendrons,²³ resulting in dendrimer—MWCNTs hybrid materials. The latter were employed as

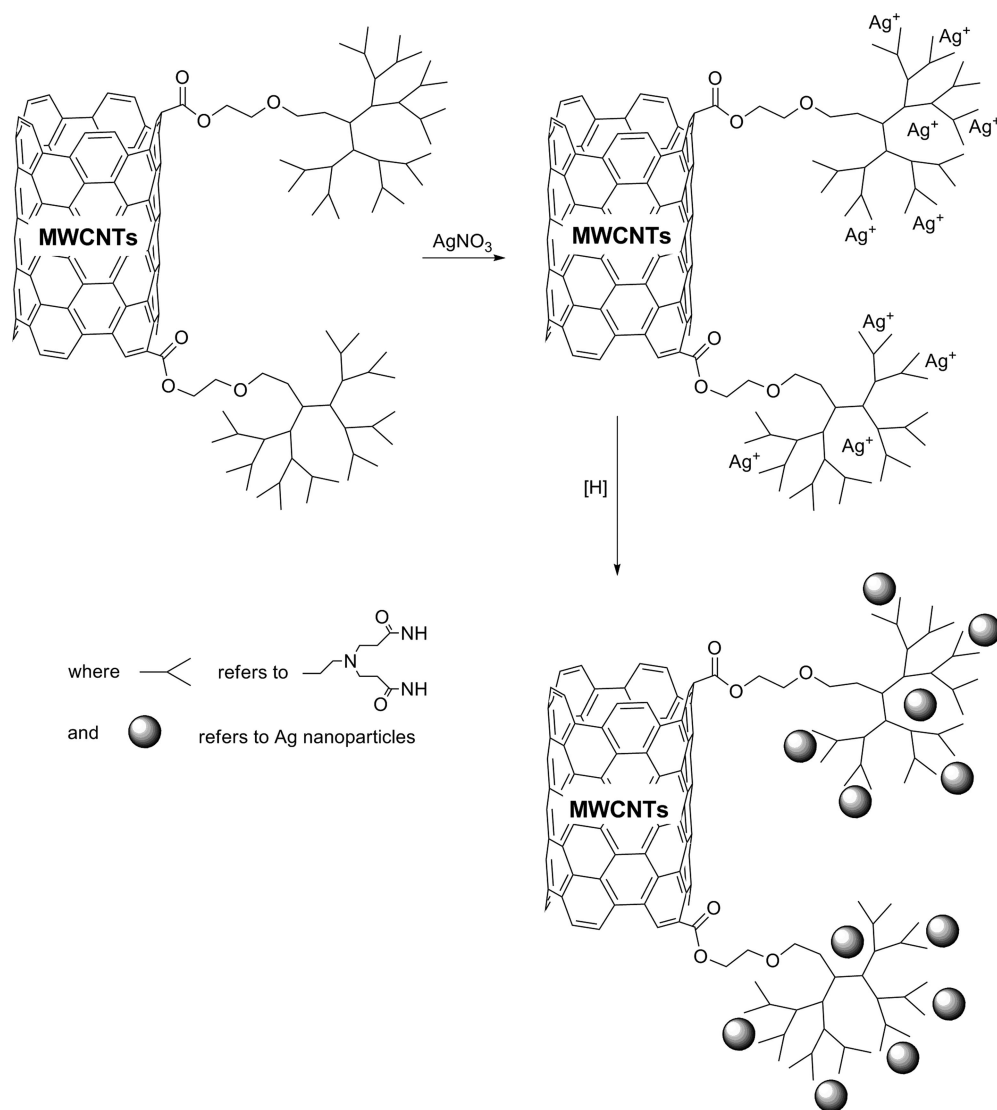


Figure 3. Decoration of PAMAM-functionalized MWCNTs with Ag nanoparticles.

templates for the deposition of silver nanoparticles, via coordination of silver(I) ions, followed by reduction with formaldehyde (Figure 3).

Moreover, Wang and co-workers²⁴ reported the direct amidation of acyl chloride SWCNTs with several primary and secondary amines, as well as with two enzymes, porcine pancrease lipase (PPL) and amino lipase (AL). In a similar way, lysine was covalently attached onto MWCNTs sidewalls, resulting in a nanomaterial that shows high dispersibility in deionized water (10 mg/mL).²⁵ Chen and co-workers²⁶ studied the polypeptide modification of CNT sidewalls and tips following the grafting-from approach. In this context, amine-functionalized tubes were used as initiating species for the ring-opening polymerization of γ -benzyl-L-glutamate *N*-carboxyanhydride (BLG-NCA), thus resulting in polypeptide-grafted MWCNTs.

In a different field of nanotechnology, shortened acyl chloride-functionalized SWCNTs were further reacted with a sterically hindered amine, such as 8-aminopentadecane, and the resulted material was used as a scaffold for the self-organization of C₆₀ molecules on the sidewall of SWCNTs. These composites were electrophoretically deposited onto a nanostructured SnO₂ electrode, and a series of microscopic and photoelectrochemical studies were performed to en-

lighten the relationship between the structures and their photoelectrochemical properties.²⁷

Prato and co-workers²⁸ employed scanning tunneling microscopy (STM) imaging to prove that the covalent functionalization of short oxidized SWCNTs with alkyl amines takes place on both the sidewalls and the tips of the nanotubes. The same research group proposed the preparation of a series of donor-acceptor SWCNT nanoconjugates, in which tetrathiafulvalene analogues were grafted as electron donors.²⁹ Similarly, Xu et al.³⁰ reported another donor-acceptor system by the amidation of acyl chloride SWCNTs with octaamino-substituted erbium bisphthalocyanine. The as-prepared material showed strong intramolecular electronic interactions, such as charge transfer from the phthalocyanine rings to SWCNTs. In the same period, Lee et al.³¹ introduced carboxylic groups onto MWCNTs by chemical oxidation, and treated them with thionyl chloride, followed by reaction with ethylenediamine, providing amino-modified MWCNTs. The latter material was further functionalized with a ruthenium(II) dye, known as an efficient photosensitizer for dye-sensitized solar cells. More recently, the functionalization of shortened carboxylated SWCNTs with strong electron acceptor photosensitizer pyrylium moieties was reported.³² The hybrid material showed a solubility increase, probably

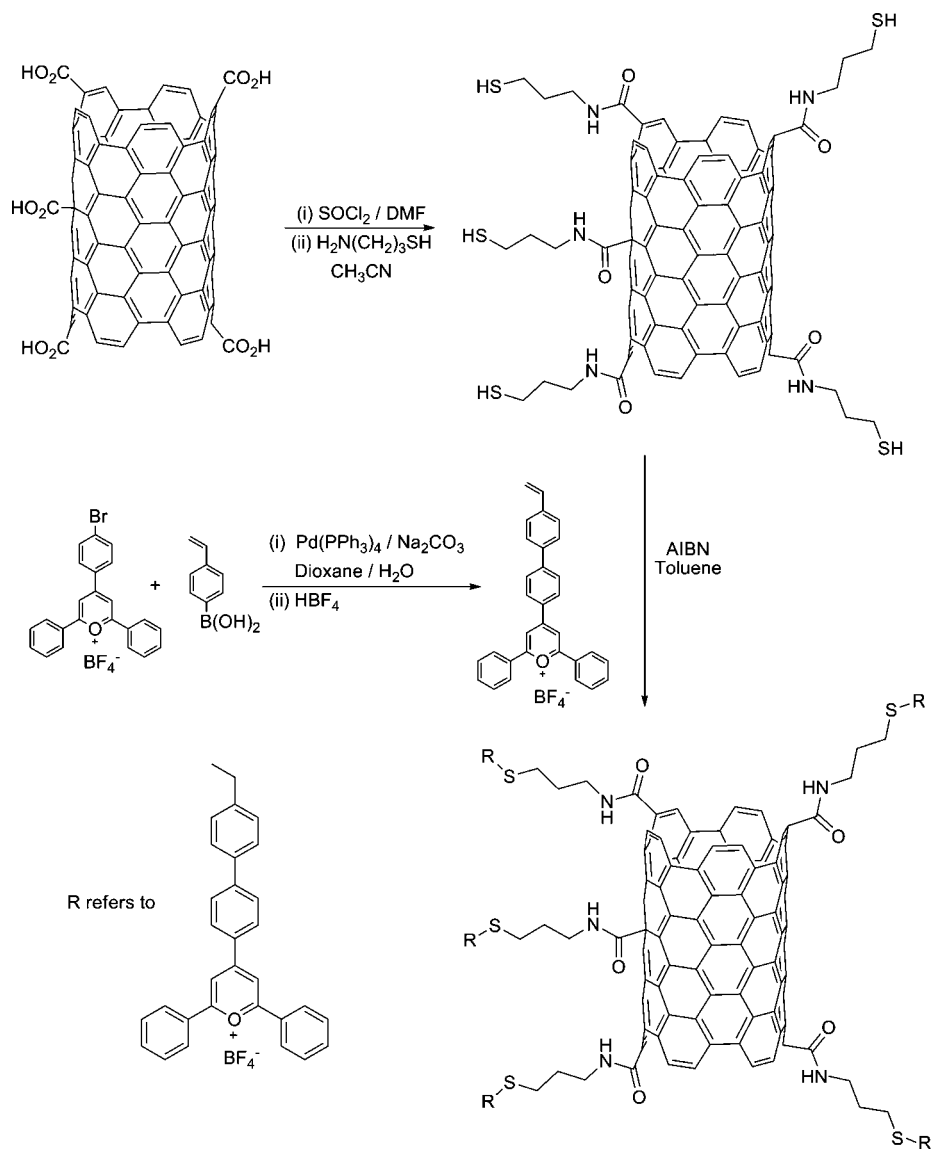


Figure 4. Illustrative synthesis of photosensitive pyrylium-functionalized SWCNTs.

derived from debundling of the pyrylium-functionalized SWCNTs as a consequence of photoinduced charge separation (Figure 4).

In another approach to obtain photoresponsive CNTs, Feng and co-workers³³ proposed the side-wall functionalization of MWCNTs with azobenzene chromophores, via amidation reaction of acyl chloride MWCNTs with diaminoazobenzene and aminododecane. The time-evolved absorption changes of the hybrid material, under irradiation of UV light, indicated that a *trans*–*cis* photoisomerization of the azo-chromophore on MWCNTs was taking place. In the same context, acyl chloride modified CNTs were further covalently functionalized with 3,4,5-tridecyloxybenzoate hydrazine, resulting in a hybrid material with good solubility and luminescent properties.³⁴

A SWCNT–fullerene conjugated hybrid was prepared via amidation of acyl chloride-functionalized SWCNTs by an amine-functionalized-fullerene derivative (Figure 5).³⁵ Subsequent esterification with *n*-pentanol on the remaining acyl-chloride groups was carried out with the aim of increasing the solubility of the obtained hybrid. High resolution-transmission electron microscopy (HRTEM) images allowed visualization of individual fullerene moieties in the ends of

the SWCNTs, and Raman spectra showed evidence of this hybridization of fullerenes and SWCNTs.

Besides acyl chloride-mediated modification of CNTs, activation of oxidized SWCNTs was also achieved with tetrachlorosilane. The resulting chlorosilylestere allow further modification on the sidewalls of the tubes, either by polyethylene glycols producing materials, which show enhanced dispersibility in water, or by encapsulated magnetic iron oxide-silica nanoparticles, which allowed the manipulation of the hybrid material in a magnetic field.³⁶

Moreover, a few other direct esterification/amidation procedures of oxidized CNTs were reported. In one of them, acid purified SWCNTs were treated with molten urea, which functions both as solvent and as reactant.³⁷ Molten urea decomposes into ammonia and isocyanic acid (HNCO), which reacts with carboxy and hydroxy groups, generated at the sidewalls and tips of the oxidized SWCNTs. Both nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements provided evidence for ureido groups attached to the resulting nanotubes, which showed excellent water solubility ($>1 \text{ g L}^{-1}$). Another research group proposed the direct thermal amidation of oxidized SWCNTs with 1,8-diaminooctane and

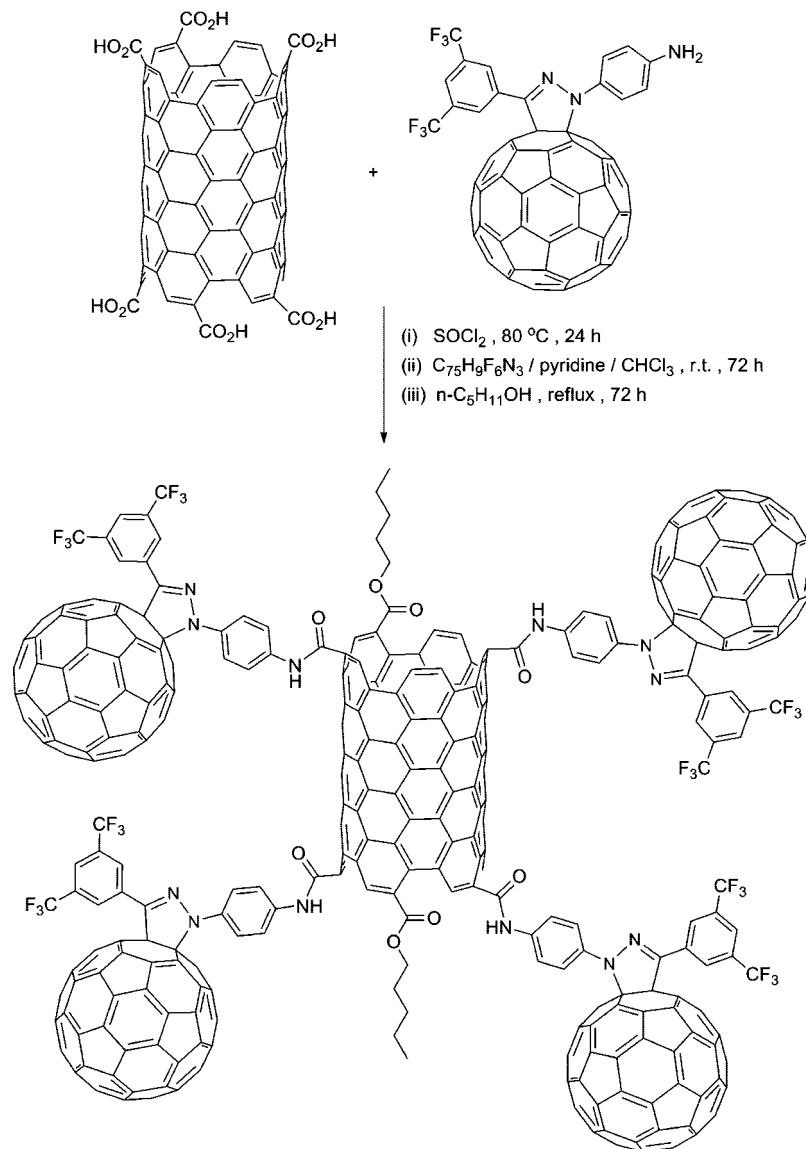


Figure 5. Synthesis of C_{60} -SWCNTs conjugated hybrid material.

further modification with L-alanine and ϵ -caprolactam under the same conditions. The reaction took place via thermal activation at $160\text{--}200\text{ }^\circ\text{C}$ instead of a chemical one, thus avoiding the use of organic solvents, and required just a few hours for completion.³⁸ Finally, acid-treated MWCNTs were covalently linked with alkyl-rich stearic acid through an esterification reaction catalyzed by H_2SO_4 . Lipophilic groups grafted on MWCNTs improved greatly the chemical affinity of MWCNTs in liquid paraffin. The as-prepared materials were shown to act as potential components in lubricating additives.³⁹

Covalent functionalization of CNTs with several organic amines was also achieved by using the well-known carbodiimide coupling chemistry. By this procedure, oxidized CNTs treated with *N*-hydroxy succinimide (NHS) or 1-hydroxy benzotriazole (HOBt), in the presence of a carbodiimide [usually *N,N'*-dicyclohexylcarbodiimide (DCC) or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC)], resulted in the formation of CNTs bearing the corresponding esters. In the final step, the esters were displaced by the amino terminal of the organic compound forming an amide linkage. A great number of substances, including several biomolecules,⁴⁰ were used for the covalent modification of CNTs. The as-prepared nanomaterials showed enhanced

solubility in organic solvents and water and were explored for several biological applications, such as components in electrochemical sensor devices.⁴¹ In particular, streptavidin, an enzyme receptor, was attached to carboxylated MWCNTs through amide bond via EDC activation and was used as an anchor for the immobilization of DNAzyme–biotin chains on the CNT sidewalls.⁴² These DNAzyme–MWCNT conjugates showed high catalytic activity and selectivity and could enable the development of cellular therapeutics that rely on the RNA cleaving ability of DNAzymes and the delivery capability of nanotubes. In an analogous work, several functionally unrelated enzymes such as horseradish peroxidase, subtilisin Carlsberg, and chicken egg white lysozyme were covalently attached onto carboxylated SWCNTs by EDC/NHS activation, producing water-soluble hybrid adducts in which the enzymes retained a high fraction of their native structure and activity upon attachment to SWCNTs.⁴³ The end-selective covalent functionalization of a mixture of oxidized PEGylated MWCNTs and SWCNTs by a 20-mer DNA capture probe was also reported. Further modification by a blue colored horseradish peroxidase-based enzymatic amplifying system was designed and took place to optimize the hybridization.⁴⁴

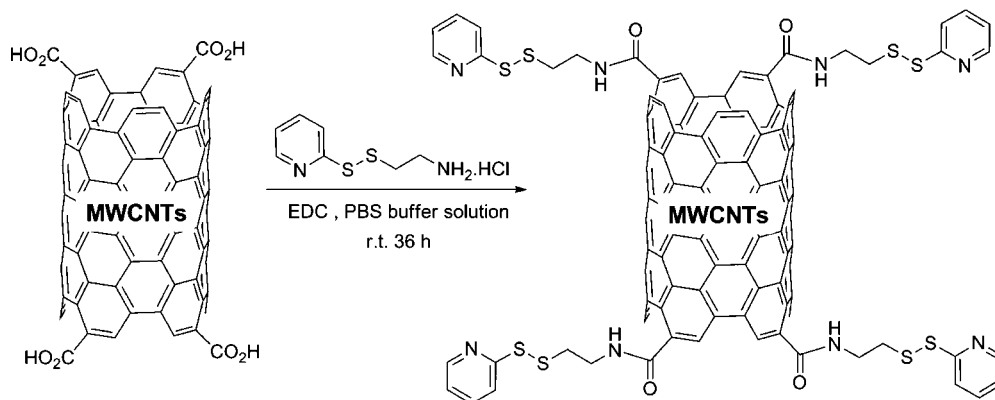


Figure 6. Derivatization of MWCNTs with pyridyldithio functionalities via carbodiimide coupling chemistry.

Using the same procedure, cysteamine, a short chain molecule with a thiol group on one end and an amine group on the other, was attached to carboxylated SWCNTs by amide bonds.⁴⁵ The covalent bonding was verified by scanning electron microscopy (SEM) imaging using gold nanoparticles of about 10 nm diameter, attached to the thiolated SWCNTs, in an aqueous solution. Furthermore, an enhanced alignment of the thiolated SWCNTs mediated by a piezoelectric surface acoustic wave field on prepatterned gold structures was demonstrated. More recently, another thiolated amine salt, the *S*-(2-aminoethylthio)-2-thiopyridine hydrochloride, reacted with carboxylated MWCNTs after EDC activation, introducing pyridyldithio functionalities onto MWCNTs sidewalls as shown in Figure 6.⁴⁶ The pyridyldithio functionalities were found to be highly reactive toward thiol through a disulfide-exchange reaction at room temperature, and the protein bovine serum albumin (BSA) was efficiently employed as a model biomolecule for this conjugation, opening a promising way to utilize many other biological molecules onto nanotubes.

Moreover, neurotrophin, an endogenous soluble protein that is regulating the differentiated functions of neurons, was covalently bound to amine-modified MWCNTs using EDC activation.⁴⁷ MWCNTs were first functionalized by amino groups through reaction of acyl chloride entities on the surface of nanotubes with 1,4-diaminobutane or 1,8-diaminooctane. In the same context, a method for the recognition of the sites of the covalent attachment of single-stranded DNA to oxidized SWCNTs was proposed by Yang and co-workers.⁴⁸ First, oxidized SWCNTs were activated either with disuccinimidylcarbonate in *N,N*-dimethylformamide (DMF) or with EDC in aqueous solution and reacted with primary amine groups on terminal ends of single-stranded DNA to form amide bonds. In a subsequent step, single-stranded DNA on gold nanoparticles was hybridized to complementary single-stranded DNA attached on SWCNTs to reveal the sites of DNA attachment to SWCNTs by TEM imaging. In an analogous study, an artificial analogue of DNA, peptide nucleic acid (PNA), was used as a linker between the SWCNTs, by functionalizing them at defect sites.⁴⁹ The dual end functionalization of PNA resulted in formation of SWCNT–PNA–SWCNT conjugates, which can be used to develop higher order assembly for molecular level electronics in future.

A variation of the EDC/NHS activated amidation of oxidized MWCNTs with green fluorescent protein (GFP) or 5-(aminoacetamido) fluorescein was developed in a water/chloroform mixture by Kouklin and co-workers.⁵⁰ A satisfactory reaction yield was achieved in the case of 5-(aminoac-

etamido) fluorescein, with reaction time and amount of surface-bound fluorescent derivative being of sufficient quantity, to observe highly dispersed functionalized CNTs. However, with GFP, a high level of bundling was observed instead. This effect was attributed to the cross-linking of CNTs with GFP, which, unlike fluorescein, has a significantly larger number of binding sites and, therefore, cross-linking efficacy.

Polyethyleneimine was also covalently attached to oxidized MWCNTs through an amide bond formation. The as-prepared MWCNTs were further modified with acetic anhydride or succinic anhydride to form MWCNTs with neutral or negative surface charges, respectively. In vitro cytotoxicity assays indicated that the biocompatibility of these functionalized MWCNTs was mainly dependent on their surface charges.⁵¹

Another interesting study was focused on the functionalization of MWCNTs with a pH-responsive dye molecule to produce a pH-sensor. Oxidized MWCNTs were activated by NHS, and 12-aminododecanoic acid was subsequently covalently grafted onto the sidewalls of MWCNTs, leaving a carboxyl-group free to react, via carbodiimide chemistry, with the hydroxy group of the dye 6,8-dihydroxy-1,3-pyrenedisulfonic acid disodium salt (DHPDS). The latter shows sensitivity in a pH range between 5.6 and 8.3, which is very common in biological systems, thus highlighting the significance of the newly prepared hybrid material. Moreover, the interaction between the MWCNTs and the dye molecule was strengthened further by noncovalent coating with an electron-donating zinc-porphyrin.⁵²

Tour and co-workers⁵³ presented the antioxidant ability of SWCNTs and ultra short SWCNTs, which were derivatized with butylated hydroxytoluene (BHT), by applying the oxygen radical absorbance capacity (ORAC) assay. The authors revealed that the antioxidant activity of modified SWCNTs depends on the kind of functionalization, for example, between the direct addition on the sidewalls of SWCNTs or further modification of the addends bearing on the sidewalls of SWCNTs via amidation bond. Thus, when the existing addends on SWCNTs were further functionalized by either covalent or noncovalent interactions with a BHT derivative, the antioxidant activity was relatively increased. On the other hand, when the functionalization of a BHT analogue is occurred directly on the sidewall of SWCNTs, the amount of BHT loading was conversely comparative to the overall antioxidant activity.

The synthesis of supramolecular nanostructures based on CNTs and ruthenium-complex luminophores was also reported.⁵⁴ Oxidized SWCNTs, activated with DCC in *N*-

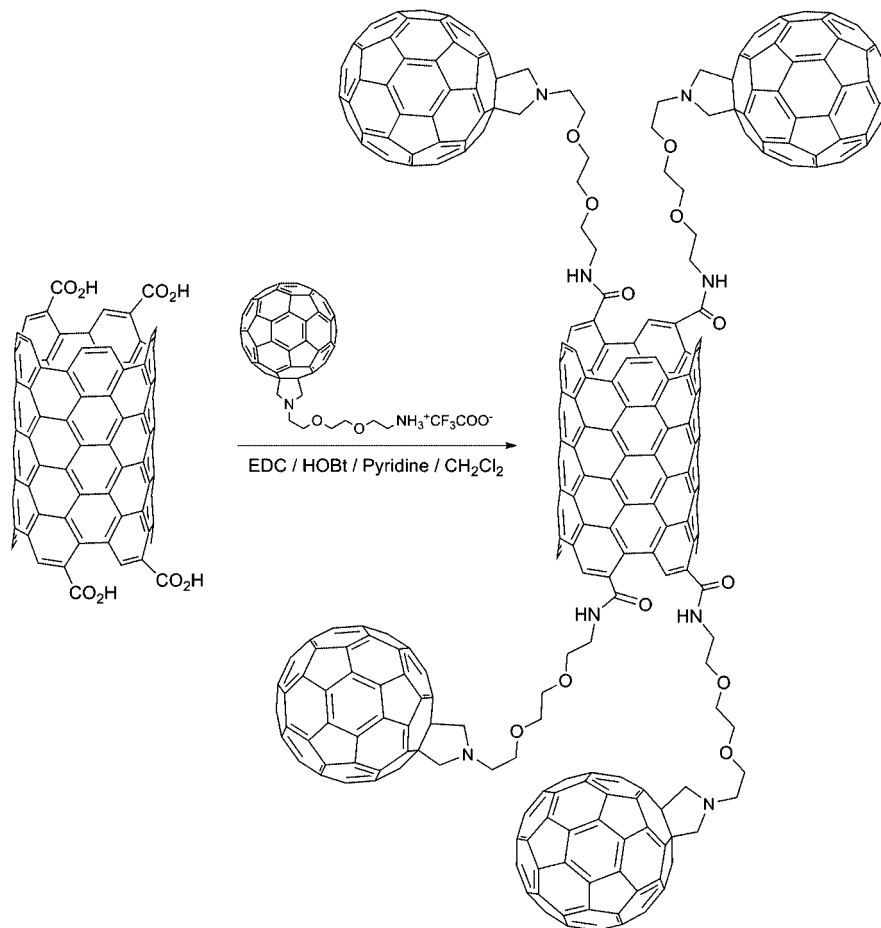


Figure 7. Derivatization of SWCNTs with C_{60} units, using carbodiimide coupling chemistry.

methylpyrrolidone (NMP) and subsequently reacted with ruthenium(4-aminophenanthroline) (2,2'-bipyridyl)₂ bis-(hexafluorophosphate), thus covalently introducing the carboxamide-tethered ruthenium-complexes. The latter functionality was found to act as light harvester by donating the excited-state electrons to the SWCNTs. In the same work, an analogous hybrid nanostructure, consisted of metallo-organic luminophore-doped silica nanobeads covalently linked to oxidized SWCNTs, was shown to have luminescent properties. Emission spectra indicated that the silica network prevented the fluorescence quenching because excited-state electrons could not be readily transferred to the SWCNT conduction band.

Thermal annealing treatment of MWCNTs, followed by refluxing in potassium permanganate solution, resulted in the introduction of carboxylic groups on the sidewalls with simultaneous purification and shortening. The as-prepared carboxylated MWCNTs were further modified by hexylamine, decylamine, and hexadecylamine, using DCC as the coupling agent, and the stability of their solutions in a great number of solvents was studied.⁵⁵

Finally, Wu et al.⁵⁶ proposed the covalent functionalization of carboxylated SWCNTs with a monomeric form of C_{60} by carbodiimide coupling chemistry (Figure 7). To achieve this, C_{60} was first modified with an amino-terminated moiety via 1,3-cycloaddition of the corresponding in situ generated azomethine ylides. Electron spin resonance (ESR) spectroscopy indicated a tendency for ground-state electron transfer from SWCNT to the C_{60} moieties in the grapevine nanostructure.

2.3. Ionic Liquids (ILs)

On the basis of a recent report, SWCNT bundles can be exfoliated in ILs to form relaxed bundles.⁵⁷ Modification of CNTs with ionic liquids is expected to improve their compatibility and stability, enhancing the potential of CNTs in applications such as sensors and actuators, by improving the electrical contact with media. Acyl chloride-functionalized MWCNTs reacted with either 1-hydroxyethyl-3-hexyl imidazolium chloride⁵⁸ or the commercially available (3-aminopropyl) imidazole, followed by the reaction with *n*-butyl bromide,⁵⁹ provided soluble functionalized MWCNTs in their ammonium form (Figure 8a,b). Transformation to other ionic liquid forms was conducted via anion exchange of the counter-anions with an excess of other target anions enhancing the solubility of the ionic liquid-functionalized MWCNTs in water and organic solvents. That kind of modification of the MWCNTs by ionic liquids changes dramatically their solubility in different solvents, depending on the anions coupled with cationic imidazole rings. Moreover, the imidazolium-functionalized MWCNTs showed a high preferential solubility in the ionic liquids, whereas the phase-transfer of the functionalized MWCNTs from aqueous solution to organic media was also achieved. In another approach, Wang et al.⁶⁰ reported the functionalization of MWCNTs with 1-(3-aminopropyl)-3-methylimidazolium bromide, via carbodiimide coupling chemistry (Figure 8c), followed by in situ reduction of $HAuCl_4$ without addition of any other reducing agents. In this frame, MWCNT surfaces were covered at high density with Au nanoparticles of average size 3.3 nm and narrow size distribution.

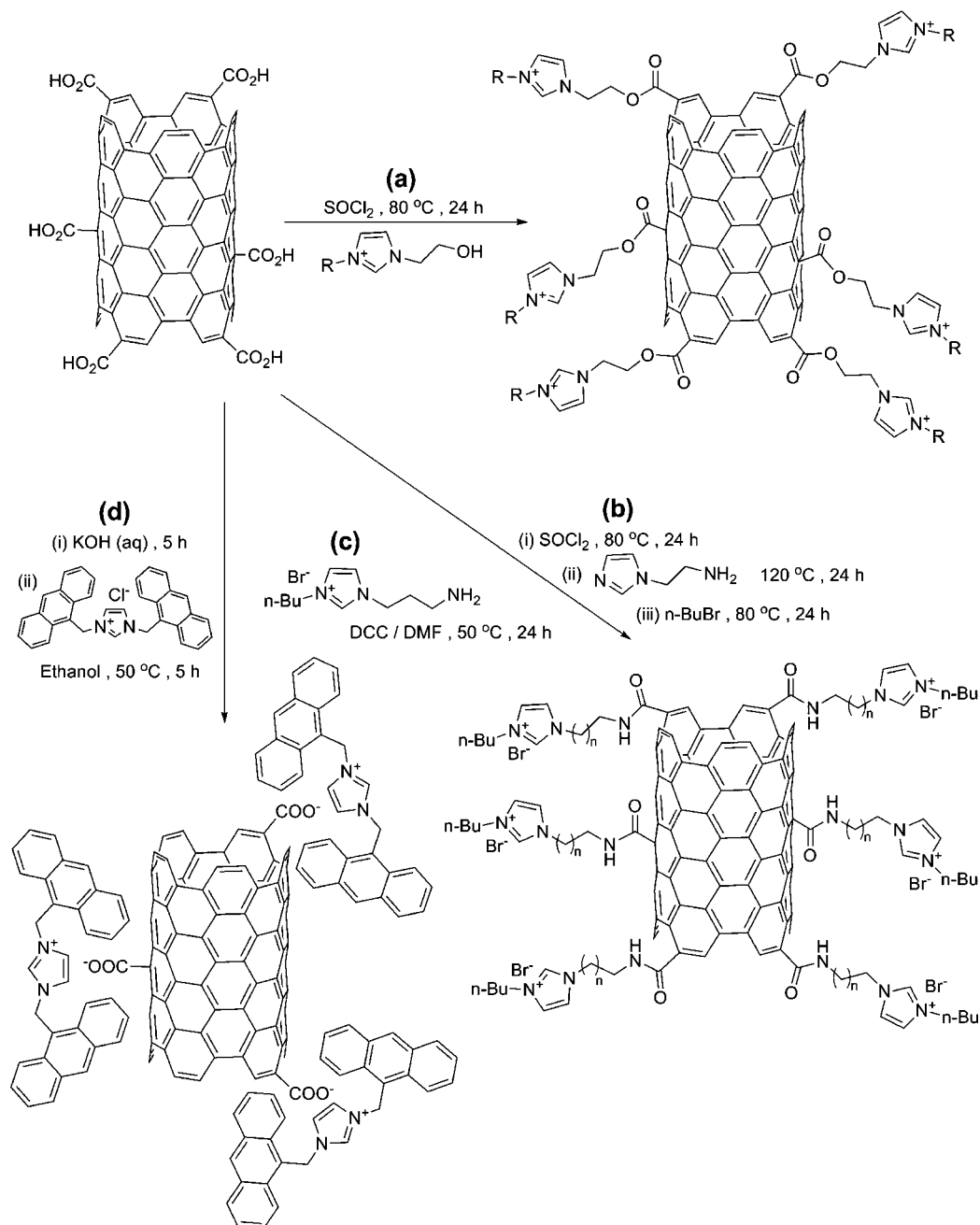


Figure 8. Modification of CNTs with imidazolium-based ionic liquids via esterification (a), amidation (b and c), and through ion exchange (d) reactions. $\text{R} = \text{C}_6\text{H}_{13}\text{Y}^-$ where $\text{Y} = \text{Cl}, \text{Br}, \text{NO}_3, \text{SO}_4, \text{CH}_3\text{CO}_2, \text{BF}_4, \text{PF}_6, \text{ClO}_4, \text{and } (\text{CF}_3\text{SO}_2)_2\text{N}, n = 1, 2$.

Moreover, the hybrid material exhibited superior electrocatalytic activity in reduction of oxygen. At the same time, Fu et al.⁶¹ proposed the attachment of the fluorescent imidazolium salt, 1,3-bis(9-anthracenylmethyl)imidazolium chloride, onto carboxylated SWCNTs, via the ion exchange mechanism (Figure 8d). The SWCNT-imidazolium covalent complex material showed blue light emission at 392, 414, and 438 nm upon being excited at 254 nm and preserved a high fluorescence quantum yield (0.4) as compared to the corresponding complex of noncovalently modified SWCNTs with imidazolium salt.

2.4. Complexation Reactions on Oxidized CNTs

The controlled self-assembly for the construction of carbon nanotube lattices with metal complexes gives rise to a new strategy for building nanomaterials that could find potential

application in nanoscale electronic devices. The self-assembly of oxidized SWCNTs was achieved on the basis of terpyridine–Cu(II) coordination, thus producing a thermally stable, neutral nanocomposite that can be quantitatively disassembled by treatment with aqueous potassium cyanide.⁶² TEM and atomic force microscopy (AFM) imaging showed clearly the mode of the possible linkages, such as head-to-head (V model), head-to-wall (T or Y models), and wall-to-wall (X model) combinations in a ratio of 5:6:1, respectively, as shown in Figure 9a.

In a similar way, the chemical functionalization of oxidized SWCNTs by organometallic chromium-centered free radicals was studied.⁶³ Free radicals were prepared by the homolytic dissociation of the (pentamethylcyclopentadienyl) chromiumtricarbonyl dimer, $[\text{Cp}^*\text{Cr}(\text{CO})_3]_2$, in a solution, at room temperature (Figure 9b). ESR and Raman spectra of the

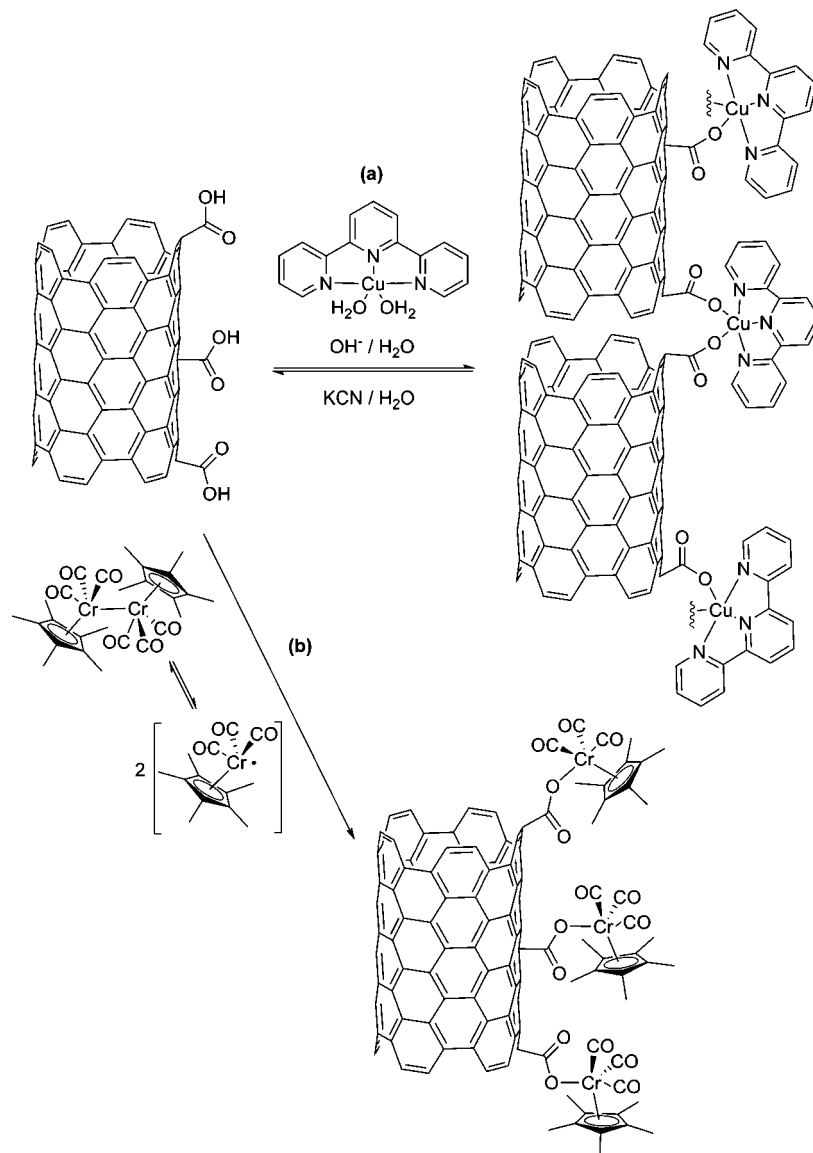


Figure 9. Modification of SWCNTs with (a) terpyridine–Cu(II) moieties and (b) (pentamethylcyclopentadienyl) chromiumtricarbonyl dimer.

functionalized material showed that chromium atom attacks irreversibly oxygen atoms on the oxidized SWCNTs (which may be carbonyl, carboxyl, or epoxide) with substantial transfer of electron density from chromium to oxygen.

In a different approach, Newkome and co-workers⁶⁴ studied the complexation of carboxylate-modified MWCNTs with hexameric metallo-macrocycles, which are based on terpyridine–metal(II)–terpyridine connectivity. The complexation of the hexamers to oxidized CNTs was successfully achieved through a cation exchange mechanism. The deposition of these rigid metallo-macrocycles onto CNT sidewalls can yield potentially useful nanohybrid structures such as photovoltaic materials, field-effect transistors, and electrochemical sensors. By an analogous mechanism, acid-treated SWCNTs were functionalized by ultrasonication in a solution of 2-trimethylammoniummethylmethane thiosulfonate (MTSET), through an ion pair formation between carboxylic anions at the SWCNT tips and ammonium cations of MTSET.⁶⁵ The authors demonstrated irreversible blocking of ion channels using these MTSET-modified tubes. In contrast, as-produced and purified SWNTs exhibited reversible blocking, indicating that the MTSET molecule attached

to SWCNTs chemically interacted with the cysteine groups in the ion channels.

2.5. Halogenation

Treatment of purified SWCNTs with peroxytrifluoroacetic acid (PTFAA) under ultrasonication gave not only oxygen-based functional groups, but also trifluoroacetic groups covalently attached to the SWCNT surface.⁶⁶ Moreover, these modified SWCNTs were shortened into ca. 300 nm length, resulting in small bundles and individual nanotubes, which were easily dispersed in polar solvents such as DMF, water, and ethanol. Barron and co-workers⁶⁷ tailored the solubility of functionalized CNTs through changing the substituent length. The authors showed that fluorinated SWCNTs could be further functionalized with α,ω -amino acids in the presence of a base catalyst, like pyridine. The aqueous solubility of α,ω -amino acid-functionalized SWCNTs may be controlled from the length of the substituent's aliphatic chain. In particular, the 6-aminohexanoic acid derivative was found to be soluble in an aqueous solution (0.5 mg mL^{-1}) in pH range 4–11, whereas the glycine and 11-aminounde-

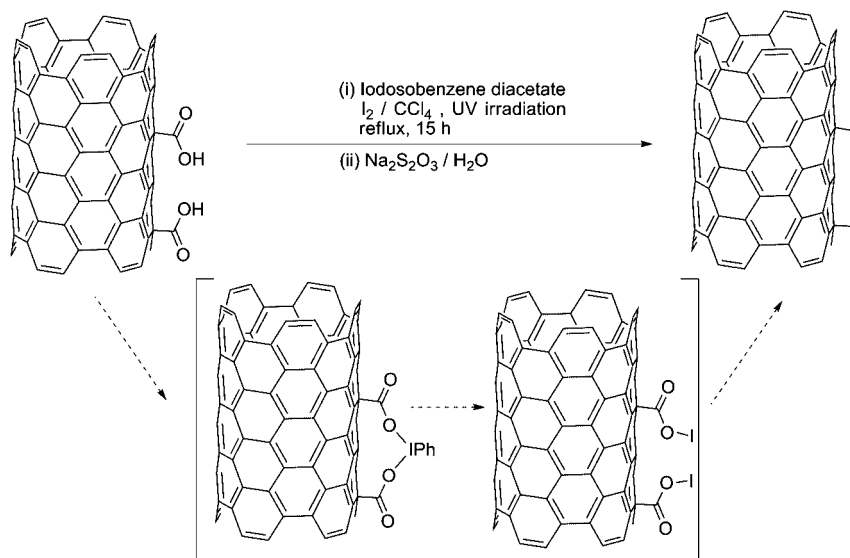


Figure 10. Iodination of SWCNTs via a modified Hunsdiecker reaction.

canoic acid derivatives are insoluble crosswise all pH values. In analogous studies, fluorinated SWCNTs were successfully functionalized with urea, guanidine, thiourea, and aminosilane moieties, which became covalently bonded on the sidewalls of SWCNTs as a result of partial substitution of fluorine atoms.⁶⁸ Spectroscopic techniques indicated that urea and guanidine reacted with the fluorinated SWCNTs through their amino groups forming carbon–nitrogen linkages with the SWCNTs sidewalls, while thiourea was attached to the sidewalls through a stable carbon–sulfur bond.^{68b}

The iodination of SWCNTs, using modified Hunsdiecker reaction conditions, was reported by Coleman et al.⁶⁹ Nitric acid treated oxidized SWCNTs reacted with idosobenzene diacetate and elemental iodine under broadband UV irradiation (Figure 10). HRTEM images showed that the unique skeleton of SWCNTs remains intact with only a small number of possible defect sites visible. Both energy dispersive X-ray (EDX) and XPS analyses confirmed the presence of iodine. The attachment of iodine atoms on the surface of SWCNTs introduces the opportunity to use metal-mediated coupling reactions for C–C bond formation with other aryl halides or large aromatic moieties.

2.6. Cycloaddition Reactions

Substituted C₂B₁₀ carborane cages were successfully attached to the SWCNT sidewalls via nitrene cycloaddition.⁷⁰ During reflux in basic conditions, the aziridine ring was opened to produce water-soluble SWCNTs in which the sidewalls are functionalized by both substituted C₂B₉ carborane units and ethoxide moieties. Selected tissue distribution studies showed that the boron atoms are concentrated specifically in tumor cells, rather than in blood and other organs. In another nitrene cycloaddition reaction, several perfluoroarylazides were used as nitrene precursors for the covalent functionalization of vertically aligned CNTs (forest). The nanoscale roughness of the forest template was utilized to make hydrophilic patterns on a hydrophobic background.⁷¹

Bingel cyclopropanation was also subjected on CNTs in past years. Thus, ultra short-SWCNTs were unbundled under strong reducing conditions and functionalized in situ with malonic acid bis-(3-tert-butoxycarbonylamino)propyl ester.⁷² The resulting nanomaterial was found to have 4–5 adducts per nanometer of nanotube length. More recently, Bingel

reaction was successfully applied for the sidewall functionalization of SWCNTs under microwave irradiation and was found to reduce the reaction time to 30 min, while increasing the amount of covalently linked substituents on the sidewalls in a controlled manner by changing the output power.⁷³

Concerning the epoxidation reaction onto CNT sidewalls, Barron and co-workers⁷⁴ studied the reaction with either trifluorodimethyldioxirane, formed in situ from trifluoroacetone and oxone (potassium peroxymonosulfate, KHSO₅), or 3-chloroperoxybenzoic acid. The authors developed a chemical approach for the quantitative determination of oxygen content in the epoxide-modified tubes by the use of triphenylphosphine as deoxygenation agent.

The well-known 1,3-cycloaddition of azomethine ylides on the sidewalls of CNTs still attracts the interest of a great number of scientists. In this context, the surface of CNTs was modified by a pyrrolidine ring, which can carry a great number of functional groups including (i) second generation PAMAM dendrimers, which were derivatized on the terminal amino group by tetraphenylporphyrins,⁷⁵ (ii) phthalocyanine addends,⁷⁶ (iii) perfluoroalkylsilane groups, which give a superhydrophobic attribute to the functionalized nanomaterial,⁷⁷ and (iv) amino ethyleneglycol groups, which were covalently bound, via carbodiimide coupling, parallel to a silicon surface via a self-assembled acid-terminated monolayer.⁷⁸ Furthermore, surface chemical functionalization of SWCNTs was carried out by introducing azomethine ylide groups containing anchored phenol structures, generated by condensation reaction of an *N*-(4-hydroxy) phenyl glycine and formaldehyde. The higher zeta potential values for these functionalized CNTs indicate their enhanced dispersibility in solvents as compared to unmodified CNTs.⁷⁹ In another example, the commercially available *N*-methylglycine and 3,4-dihydroxybenzaldehyde were used for the 1,3-dipolar cycloaddition reaction on SWCNTs and provided stable dispersions of modified SWCNTs in a range of polar solvents, including water.⁸⁰ Moreover, a mild and efficient method for the selective modification of semiconducting SWCNTs, by cycloaddition of azomethine ylides derived from trialkylamine-*N*-oxides, was reported by Mioskowski and co-workers.⁸¹ This was achieved by preorganizing the starting *N*-oxides on the nanotube surface prior to generating the reactive ylides. Separation of metallic SWCNTs from

functionalized semiconducting SWCNTs was successfully accomplished by inducing solubilization of semiconducting SWCNTs in the presence of lignoceric acid through the formation of alkyl ammonium functionalities in the pyrrolidine ring.

In an alternative approach, the microwave-assisted thermal cycloaddition of azomethine ylides introducing 4-octadecyloxyphenyl pyrrolidine groups to the sidewalls of MWCNTs was found to be 50–60 times faster than the one using the conventional reaction conditions.⁸² Similarly, Prato and co-workers⁸³ proposed microwave irradiation to rapidly functionalize CNTs by using 1,3-dipolar cycloaddition of aziridines. An indirect proof of the covalent sidewall functionalization was provided by the thermal retro-cycloaddition of pyrrolidinofullerenes, which took place when the modified CNTs were heated in the presence of a catalyst, in the presence of an excess of C₆₀ to trap the corresponding ylide. More recently, the same research group proposed the double functionalization of CNTs by 1,3-dipolar cycloaddition and addition of diazonium salts under microwave conditions.⁸⁴ In an analogous approach, the microwave-assisted 1,3-dipolar cycloaddition of a 4-pyridyl nitrile oxide to the sidewalls of modified SWCNTs having pentyl ester groups at their tips resulted in the formation of a doubly functionalized material with enhanced solubility in organic solvents.⁸⁵ This material formed complexes with a zinc-porphyrin via coordination of the 4-pyridyl group with the metal. Steady-state fluorescence and nanosecond transient spectroscopy indicated an energy transfer quenching of the zinc-porphyrin singlet excited state by 4-pyridyl isoxazolino-SWCNTs but no evidence for the occurrence of electron transfer.

By the 1,3-dipolar cycloaddition of azomethine ylides onto sidewalls of CNTs, the carbon nanostructures were shown to be functionalized with bioactive peptides, proteins, nucleic acids, and drugs and used to deliver their cargos to cells and organs. Because of the low toxicity of functionalized CNTs, in sharp contrast with pristine CNTs,⁸⁶ such systems showed great potential in the field of nanobiotechnology and nanomedicine.⁸⁷ In that frame, Bianco and co-workers proposed the covalent functionalization of MWCNTs via 1,3-dipolar cycloaddition of azomethine ylides, with protected amino groups that can be selectively deprotected and subsequently modified with biomolecules such as amphotericin B, a known antifungal antibiotic,⁸⁸ and methotrexate, an anticancer drug.⁸⁹ These hybrids were able to enter a cell by a penetration mechanism acting as a drug delivery system. Further coupling with a fluorescent moiety like fluorescein isothiocyanate can help the monitoring of the hybrid material into the cells. Moreover, the interaction between pyrrolidino-functionalized CNTs with neuronal cells was investigated, indicating that CNTs can encourage neuronal electrical activity in networks of cultured cells by constructing tight contacts with the cell membranes that might favor electrical shortcuts between the central and farthest areas of neuron.⁹⁰ It was also presented that such conjugates carrying cell-adhesion peptides show no affection on neuronal morphology, viability, and function, thus representing CNTs as a promising applicant for the development of novel drug carriers.⁹¹

In an analogous study, SWCNTs were functionalized with a chelating molecule, diethylenetriaminepentaacetic acid (DTPA), and labeled with radiolabeled indium (¹¹¹In) for imaging purposes.⁹² Intravenous administration of these

functionalized SWCNTs in rats followed by radioactivity tracing indicated that the tubes were not retained in any of the reticuloendothelial system organs (liver or spleen) and were rapidly cleared from systemic blood circulation through the renal excretion route. The observed rapid blood clearance and half-life (3 h) of modified tubes showed major implications for all potential clinical uses of CNTs. Moreover, urine excretion studies using both functionalized SWCNTs and MWCNTs followed by electron microscopy analysis of urine samples revealed that both types of nanotubes were excreted as intact nanostructures. By using pyrrolidine-modified CNTs with appended ammonium groups, Kostarelos and co-workers⁹³ developed a simple methodology to correlate the aggregation state of tubes with the intensity of their fluorescence in the UV–vis spectrum. Similarly, confocal laser scanning microscopy was utilized to localize optically the CNT material into mammalian cells.⁹⁴

The Diels–Alder cycloaddition is also known to take place on the sidewalls of CNTs. Fluorinated SWCNTs were shown to undergo a facile Diels–Alder cycloaddition with several dienes, such as 2,3-dimethyl-1,3-butadiene, anthracene, and 2-trimethylsilyloxy-1,3-butadiene, resulting in highly functionalized SWCNTs. The presence of electron-withdrawing fluorine atoms on the surface of SWCNTs was suggested to activate the double bonds on the SWNT sidewall, enhancing the rate of cycloaddition reaction.⁹⁵ An alternative method, developed by Mioskowski and co-workers,⁹⁶ was based on the simultaneous activation of the Diels–Alder cycloaddition using high pressure (1.3 GPa) in the presence of a transition metal complex (chromium hexacarbonyl). Supplementary experiments showed that there was a synergistic effect of pressure and chromium complex for the successful CNT modification. More recently, theoretical calculations on the functionalization of chiral and nonchiral SWCNTs through Diels–Alder [4 + 2] cycloaddition were performed,⁹⁷ while various substituted benzocyclobutenes were used for the controlled functionalization of MWCNTs.⁹⁸ The extent of functionalization, in bulk and in solution at different temperatures, was investigated. Chang and co-workers demonstrated that MWCNTs can serve as either a dienophile or a diene in Diels–Alder reactions.⁹⁹ Briefly, they managed to employ a furan derivative, carrying electron-withdrawing substituents, as a diene reagent, to modify MWCNTs through a Diels–Alder cycloaddition, and in a similar approach they utilized a maleimide compound as a dienophile for the covalent functionalization of MWCNTs. Another cycloaddition approach used a zwitterion moiety, resulting from the addition of 4-aminopyridine (DMAP) to dimethyl acetylenedicarboxylate (DMAD).¹⁰⁰ A positively charged five-membered ring intermediate was formed on the sidewalls of SWCNTs (Figure 11). The addition of a second nucleophile, such as methanol or 1-dodecanol, replaced the DMAP moiety by an alkoxy group, thus providing the functionalized SWCNTs. Varying the electrophile from DMAD to other substituted esters resulted in intermediates with chloroethyl, allyl, and propargyl functional groups on the sidewalls of CNTs, which can further undergo S_N2 substitution, thiol addition, or 1,3-dipolar cycloaddition reactions. Moreover, alterations on the cyclopentenones bearing on the CNTs led to hydrolyzed products, with high solubility in water.^{100b} The covalent grafting of cobalt(II) porphyrin moieties onto modified MWCNTs via zwitterionic functionalization was also reported. When the as-prepared composite was mixed with Nafion, it displayed an excellent electrocatalytic per-

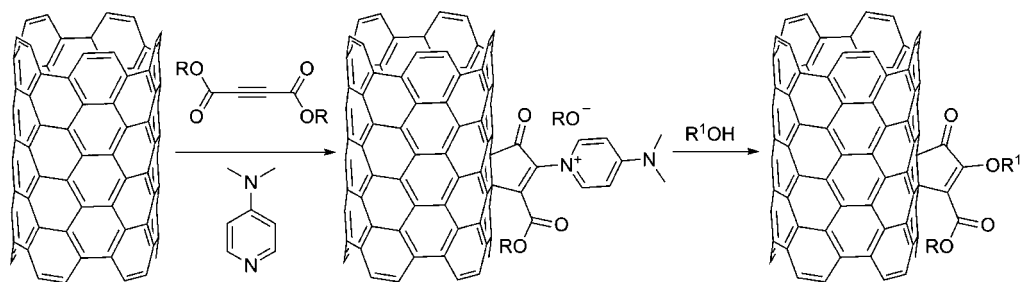


Figure 11. Modification of SWCNTs via dimethyl acetylenedicarboxylate-4-dimethylaminopyridine zwitterion method ($R =$ chloroethyl, allyl, propargyl, and $R^1 =$ methyl, dodecyl).

formance for oxygen reduction in acidic media at room temperature.^{100c}

Finally, the reaction between MWCNTs and 3,6-diaminotetrazine under heating was investigated. Several possible interactions, including cycloaddition, cross-linking reactions, and coating of the nanotubes through π - π interactions, depending on the reaction time, were observed.¹⁰¹

2.7. Radical Additions

Tour and co-workers were the first who proposed the covalent sidewall modification of CNTs via in situ generated aryl diazonium salts, providing highly functionalized and well-dispersed hybrid materials in organic solvents and water. In past years, some theoretical approaches¹⁰² and several experimental variations and improvements of the already utilized procedures were proposed, whereas studies were held to explain the mechanism and the selectivity of the reaction.¹⁰³ In particular, the functionalization of SWCNTs with aniline derivatives using sodium nitrite in a mixture of 96% sulfuric acid and ammonium persulfate, instead of the corrosive and hazardous oleum, was reported by Stephenson et al.¹⁰⁴ However, an even milder procedure consisting of vigorous stirring of CNTs “on water” in the presence of a substituted aniline and an oxidizing agent was investigated by Price et al.,¹⁰⁵ while, more recently, a solvent-free procedure was proposed by Chen et al.¹⁰⁶ By using organic triazene compounds as stable precursors to diazonium salts, the group of Tour showed that the functionalization of SWCNTs was facilitated in aqueous solutions.¹⁰⁷ Water-soluble sulfonated SWCNTs, prepared by diazonium chemistry in oleum, were shown to react repetitively with numerous diazonium salts in water.¹⁰⁸ By using this repetitive functionalization protocol, the authors prepared multifunctional SWCNTs containing moieties that would not be stable to the harsh oleum functionalization conditions used in the first step.

In a similar approach, a very mild, rapid, and environmentally friendly method for the radical functionalization of SWCNTs involved the room temperature grinding of

CNTs for several minutes with various aryldiazonium salts in the presence of potassium carbonate and imidazolium-based ionic liquids as the solvent medium¹⁰⁹ (Figure 12). An analogous environmentally friendly, rapid, and inexpensive method for the covalent sidewall modification of SWNTs involved the use of molten urea as the solvent.^{109b}

In a recent study, covalently linked CNTs by using methylenedianiline as diazonium salt precursor were spun in the form of microfibers and used as scaffolds for hydrogen storage.¹¹⁰ These 3-D nanoengineered fibers were found to physisorb twice as much hydrogen per unit surface area as do typical macroporous carbon materials. Darabi et al. proposed the covalent attachment of a thioamide group to the sidewalls of carbon nanotubes in two steps. First, the diazonium salt chemistry was followed, employing 4-acetylaniline, for the generation and the direct covalent attachment of acetophenone moieties onto SWCNTs. In a second step, following the protocol of the Willgerodt–Kindler reaction, the acetophenone moieties bearing on SWCNTs were reacted with sulfur and morpholine in DMF to give the terminal thiomorpholides.¹¹¹

In another study, the chemical modification of SWCNTs with diazonium salts bearing electrowithdrawing groups resulted in hybrid materials that allow the identification of the characteristic signatures of the addends by electrochemistry, and this can prove as an advantageous technique for the qualitative analysis of SWCNTs functionalization.¹¹²

Concerning the fabrication of donor–acceptor systems, Guo et al.¹¹³ prepared a novel CNT–porphyrin nanohybrid that was prepared by the covalent modification of SWCNTs via in situ generated porphyrin diazonium compounds and showed superior optical limiting effects for nanosecond laser pulses. In a similar approach, Campidelli and co-workers suggested the functionalization of SWCNTs with 4-(trimethylsilyl)ethynylaniline by applying diazonium chemistry and the subsequent attachment of either a zinc-phthalocyanine derivative or a zinc-porphyrin dendron using a modified Huisgen 1,3-dipolar cycloaddition.¹¹⁴ The functionalization of SWCNTs with imidazole derivatives, like 2-(4-aminophe-

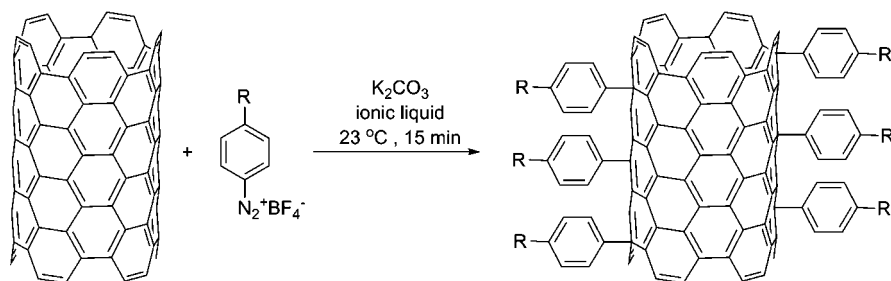


Figure 12. Mild functionalization of SWCNTs with aryldiazonium salts in the presence of ionic liquids. $R =$ F, Cl, Br, I, NO_2 , *t*-butyl, CO_2CH_3 , or $\text{C}\equiv\text{CH}$.

nyl)-4,5-diphenylimidazole, led to highly soluble hybrids materials, which show weak intramolecular electronic interactions between the nanotubes and the imidazole groups covalently attached to the skeleton of the SWCNTs.¹¹⁵

In another approach, water-soluble-functionalized SWCNTs via diazonium chemistry showed significant orientation in very weak magnetic fields,¹¹⁶ while the corresponding modified MWCNTs were subjected in toxicological *in vitro* investigations.¹¹⁷ These essays indicated that functionalization of nanotubes decreased dramatically their toxicity profile.

Functionalized CNTs by diazonium chemistry have been widely used as scaffolds for further modification. In that context, the first Suzuki coupling reactions were reported on iodophenyl-functionalized SWCNTs, resulting in covalently connected π -conjugated porphyrin, fluorene, and bithiophene chromophores.¹¹⁸ This kind of chemistry showed a great potential in fabricating SWCNT-based photo- and electroactive materials. Iodophenyl-functionalized SWCNTs were also used as a precursor in Heck cross-coupling reactions for the grafting of several acrylates carrying photosensitive moieties on the sidewalls of prefunctionalized CNTs.¹¹⁹ Importantly, the covalent linkage between CNTs and the chromophores does not introduce new photochemical processes but only modulates the strength and life of the photogenerated transients, which are equally observed when there is no covalent bond between the components. In another example, self-assembly of functionalized SWCNTs with aryl diazonium salts was performed on silicon,¹²⁰ silver,¹²¹ aluminum/aluminum oxide,¹²² or hafnium oxide¹²³ surfaces, leading to high performance field-effect transistors and providing the possibility of large-scale integration in other electronic, optical, and sensor arrays. Ellison and Gasda proposed the covalent functionalization of SWCNTs with a phenyl amine group using 1,4-benzenediamine as a precursor in a diazonium reaction protocol.¹²⁴ The amine group on the functionalized SWCNTs can further react with succinimidyl-4-(*N*-maleimidomethyl)cyclohexane-1-carboxylate (SMCC), which was previously used as a DNA linker. In a similar way, water-soluble 4-carboxyphenyl modified SWCNTs were further functionalized with a nitrilotriacetic ligand that can complex nickel for directing the reversible self-assembly of polyhistidine-tagged proteins onto the nanotube surface at controlled orientation.¹²⁵ Concerning the detachment of aryl moieties from the CNT sidewalls, besides thermal treatment, an alternative method was reported by Lim et al.,¹²⁶ in which the authors used UV laser irradiation.

Besides the functionalization of CNTs via *in situ* generation of diazonium salts, several other techniques that involve surfactant-mediated, thermal, or photochemical radical additions on the sidewalls of CNTs were performed. Thus, Murata and co-workers reported the sidewall amino-functionalization of SWCNTs by organic hydrazines, proceeding in an aqueous surfactant solution, at ambient temperature.¹²⁷ The degree of functionalization, as designated by Raman spectra, was enhanced by raising the concentration of surfactant and also depended on the substituent on the hydrazine (phenyl, 4-methoxyphenyl, 4-bromophenyl, and 4-nitrophenyl). The as-prepared material is soluble in organic solvents up to 100 mg/L. Moreover, the covalent functionalization of SWCNTs from *p*-methoxyphenyl radicals, generated by thermal air oxidation of 4-methoxyphenylhydrazine, was also reported.¹²⁸ The same reaction was also investigated under microwave conditions. With a similar yield of functionalization, the microwave-assisted reaction showed to be

far more rapid with an optimal time of around 5 min, whereas thermal treatments are often measured in days.¹²⁹ Furthermore, deprotection of the methoxy groups of the *p*-methoxyphenyl-SWCNTs generated free alcohol groups, and, finally, esterification with acryloyl chloride introduced a double bond for initiating a polymerization process.¹³⁰

By using a simple approach, Wei et al.¹³¹ studied the thermal reaction between potassium and benzophenone in the presence of CNT material. It was shown that electron transfer from potassium atom to benzophenone produced a carbon radical that could be readily added to the surface of SWCNTs, leading to their decoration by diphenylcarbinol moieties. In an analogous study, Billups and co-workers observed the thermal decomposition of four diacyl peroxides (benzoyl, 4-methoxybenzoyl, phthaloyl, and trifluoroacetyl) in the presence of SWCNTs.¹³² They found that among the four tested, phthaloyl peroxide could functionalize SWCNTs to the greatest extent with the benzoyl peroxide following after. Phenyl-modified CNT material produced by the thermal dissociation of benzoyl peroxide was used for the fabrication of water-soluble tubes.¹³³ The sulfonation of phenyl-functionalized SWCNTs in oleum provided a scalable method for the preparation of fully debundled CNTs in aqueous media. To introduce carboxylic moieties onto CNT sidewalls, Stellacci and co-workers¹³⁴ applied a variation of the previous approach, which involved the solvent free thermolysis of succinic acyl peroxide in the presence of SWCNTs.

The mild photochemical silylation of SWCNTs with trimethoxysilane and hexaphenyldisilane precursors was presented by the group of Wong.¹³⁵ Specifically, for the trimethoxysilane addition with the presence of $-\text{Si}(\text{OCH}_3)$ groups, a Si–O–Si network was created along the sidewalls on the nanotube framework. As for the hexaphenyldisilane addition, the attachment of $-\text{Si}(\text{Ph})_3$ groups to oxygenated functionalities onto the ends and defect sites of the nanotube was observed. The as-prepared SWCNTs showed enhanced solubility in DMF. In another work, Maeda et al.¹³⁶ presented the preparation of SWCNTs–organosilicon hybrid materials after irradiation with a low-pressure mercury-arc lamp of a benzene suspension containing SWCNTs and a disilane. The silylation of SWCNTs significantly increased their field emission properties. In an analogous study, the photolysis of acetonitrile in the presence of SWCNTs resulted in the sidewall modification of the surface by amino functional groups via a radical reaction.¹³⁷ These modified SWCNTs were used as anchors for the attachment of silver nanoparticles on the sidewalls of SWCNTs. Finally, Alvarez et al.¹³⁸ proposed the selective photochemical hydroxylation of semiconducting and small diameter metallic SWCNTs by 254 nm UV irradiation in acidic, neutral, and basic aqueous solutions at ambient and elevated temperatures, while the photochemical hydroboration of SWCNTs with a variety of borane complexes in a wavelength range of 250–300 nm was also reported.¹³⁹

Billups and co-workers¹⁴⁰ studied extensively the reductive lithiation of SWCNTs in liquid ammonia. This approach yielded a dispersion of CNT-based salts, which could react with alkyl/aryl halides, alkyl/aryl sulfides, or aryl disulfides to produce partially debundled SWCNTs functionalized by alkyl or aryl moieties. These reactions followed a pathway in which a single electron is transferred to the halide to form a transient radical anion that then dissociates into a carbon-centered free radical and halide. The specific surface areas of the functionalized nanotubes were measured,¹⁴¹ while

further investigations showed that the reaction is dependent on the SWCNTs diameter and that the functionalization of metallic over semiconducting CNTs is preferred.¹⁴² The group of Tour utilized this method to introduce several alkyl and aryl groups on the sidewalls of MWCNTs, producing functionalized material that was soluble in either organic or aqueous solvents.¹⁴³ A modified route using lithium in liquid ammonia, or lithium naphthalenide in tetrahydrofuran at ambient temperature, was also used for the functionalization of SWCNTs with alkyl groups.¹⁴⁴ Finally, García-Gallastegui et al.¹⁴⁵ demonstrated that catalytic amounts of di-tert-butylbiphenyl can act as electron carrier and efficiently promote the formation of carbanionic SWCNTs from pristine SWCNTs and lithium. When the reduction reaction was carried out in the presence of acrylic ester monomers, different polyacrylate-SWCNTs were obtained.

2.8. Nucleophilic Additions

Hirsch and co-workers utilized the nucleophilic addition of organolithium and organomagnesium compounds on the sidewalls of SWCNTs producing highly exfoliated negatively charged intermediates, which, after subsequent air reoxidation, lead to neutral, unbundled, and highly functionalized SWCNTs by alkyl moieties.¹⁴⁶ This reaction showed pronounced selectivity of metallic toward semiconducting SWCNTs because of the availability of electronic states close to the Fermi level. Moreover, the reactivity of SWCNTs toward the addition of organometallic compounds was found to be inversely proportional to the diameter of the tubes and depended on the steric demands of the addend. The same research group has also demonstrated the nucleophilic SWCNT-sidewall addition of amine-based nucleophiles, in situ generated lithium amides leading to amino-functionalized SWCNTs, which exhibit a drastically improved solubility in organic solvents.¹⁴⁷

2.9. Electrophilic Additions

The electrophilic addition of alkylhalides onto SWCNTs with the aid of microwave irradiation resulted in the attachment of alkyl and hydroxyl groups onto the surface of the nanotubes. These alkyl groups were shown to enhance the interaction between the modified SWCNTs and polymer molecule chains, while the hydroxy groups can be further esterified with acyl halide to obtain the corresponding ester derivatives of SWCNTs.¹⁴⁸

In another approach, Tessonier et al.¹⁴⁹ presented the covalent attachment of amino groups directly on the structural defect sites of the surface of MWCNTs, based on a deprotonation–metalation procedure, with the aid of excess of butyl lithium, followed by an electrophilic substitution. This procedure outclasses the classical oxidation–amination route and results in very homogeneous samples, with a high number of amino groups, which were used as model heterogeneous catalysts in the synthesis of biodiesel.

Friedel–Crafts acylation of SWCNTs has been reported by Balaban et al.,¹⁵⁰ employing either nitrobenzene as a solvent at 180 °C and aluminum chloride as a molar reactant or an aluminum chloride/sodium chloride melt at 180 °C. A mild, less destructive Friedel–Crafts acylation of MWCNTs, by 4-substituted benzoic acids, has been also achieved, using a mixture of polyphosphoric acid and phosphorus pentoxide as reaction media.¹⁵¹

2.10. Electrochemical Modifications

Electrochemistry signifies an excellent tool for nanotube functionalization. The selective functionalization of individual contacted metallic SWCNTs with electrochemically generated aminophenyl radicals was achieved, and the fabrication of a CNT-based pH sensor was demonstrated.¹⁵² In an analogous study, the electrochemical nitration of SWCNT sheets with nitro groups was achieved using a 6 M aqueous solution of potassium nitrite, which was anodically oxidized.¹⁵³

Sacher and co-workers¹⁵⁴ studied the chemical and morphological modification of MWCNTs by 2 keV Ar⁺ treatment. The modified tubes were characterized by field emission-SEM, HRTEM, XPS, and Raman spectroscopies. These studies demonstrated the creation of free radical defects and the amorphization of MWCNTs with an Ar⁺ dose of as little as 10¹³ ions cm⁻². Higher doses caused the loss of material through fragmentation.

In a similar approach, Ramanath and co-workers¹⁵⁵ extended the functionalization of CNTs by focused-ion-beam irradiation. The authors showed that nanoparticles, fluorescent microspheres, an amino acid, or a metalloprotein could be assembled on CNT surface without aggressive wet chemical oxidation. These functionalities were anchored by electrostatic and covalent interactions onto ion-irradiated MWCNTs.

2.11. Plasma-Activation

Inductive coupled radio frequency plasma was used to modify MWCNTs. The variation of diverse plasma parameters on the functionalization of MWCNTs, such as type of gas, treatment time, pressure, and position of the sample inside the reaction chamber, was systematically studied. Various plasma gases were used, such as O₂ to graft hydroxyl, carboxyl, and carbonyl groups; NH₃ for amines, nitriles, and amide groups; and CF₄ for fluorine atoms.¹⁵⁶ CF₄ plasma fluorinated SWCNTs were further modified with 1,2-diaminoethane, creating n-type SWCNTs devices.¹⁵⁷ Moreover, plasma pretreated MWCNTs were used as scaffolds for the deposition of metal clusters through thermal evaporation of Au, Ag, or Ni atoms in vacuum conditions.¹⁵⁸ The evolution of shape, dispersion, and size of the nanoparticles onto the modified CNTs was studied by TEM and XPS spectroscopies.

Microwave-generated nitrogen plasma was found to be a suitable source for introducing nitrogen functional groups onto SWCNTs and MWCNTs sidewalls.¹⁵⁹ The as-prepared functionalized MWCNTs material was used to fabricate a photovoltaic device, which showed a better performance than the one fabricated with pristine MWCNTs.¹⁶⁰ Such amine-modified MWCNTs were also shown to act as efficient initiators for the polymerization of lactone monomers.¹⁶¹ Furthermore, nitrogen-doped MWCNTs were also used as scaffolds for the deposition of PtRu nanoparticles, which were used as catalysts for the electrooxidation of methanol.¹⁶²

A method for the functionalization of SWCNTs by argon plasma-assisted UV grafting of 1-vinylimidazole was reported by independent studies.¹⁶³ Purified SWCNTs were exposed to argon plasma for the generation of defect sites at the tube ends and sidewalls. These can act as the active sites for the motivated by UV irradiation attachment of 1-vinylimidazole. No visible cutting of the functionalized SWNT was observed, by controlling the time and the energy

of argon plasma treatment, while AFM measurements showed that SWCNTs bundles exfoliate to individual tubes after the grafting.

In another work, atmospheric pressure plasmas (APP) were suggested to be particularly suitable for functionalization of aligned nanotubes, where wet chemical manipulation could damage the vertical alignment.¹⁶⁴ A detailed experimental study elucidating the effects of air-atmospheric pressure dielectric barrier discharge (APDBD) plasma treatment parameters (e.g., power density, discharge composition, interelectrode gap, and treatment time) on the electronic structure, physical, and chemical behavior of carbon nanotubes was conducted. XRD and neutron diffraction, TGA, Raman, and XPS techniques were used for the material characterization.

More recently, Imasaka et al.¹⁶⁵ reported the preparation of water-soluble MWCNTs and SWCNTs by using a pulsed streamer discharge, generated in a suspension of CNTs in water. The repetitive pulsed streamer discharge was generated by applying multiple square voltage pulses to a needle to plane electrode system immersed in the CNT suspension. The hydroxyl moieties bound to the CNT surface, which were identified by FTIR spectroscopy, seemed to be responsible for the solubilization effect. The hydroxylic groups might be formed by chemical reactions between O and H radicals, which were detected by optical emission spectroscopy.

Surface modification of MWCNTs in a large scale was also reported utilizing oxygen plasma treatment.¹⁶⁶ In that work, homemade equipment consisting of a rotating barrel fixed between the two discharge electrodes was used. XPS and SEM analyses showed that modification of MWCNTs strongly depended on the power and the time of plasma treatment.

2.12. Mechanochemical Functionalizations

Baibarac et al.¹⁶⁷ studied the behavior of SWCNTs under nonhydrostatic compression at 0.58 GPa, either alone or dispersed into various matrices. SWCNTs were found to break in fragments of different size due to the compression process. When matrices such KI and Ag were used, donor–acceptor complexes were formed. Alternatively, in aromatic hydrocarbons like biphenyl or *p*-terphenyl matrices, an ionic and covalent functionalization of SWCNTs fragments was demonstrated by surface enhanced Raman spectroscopy. In a different mechanochemical approach, Li et al.¹⁶⁸ used a high-speed vibration mill for the side functionalization of SWCNTs with alkyl and aryl groups. Similarly, the surface chemical functionalization of SWCNTs, DWCNTs, and MWCNTs was also carried out by reaction of CNTs with potassium hydroxide in ethanol, at room temperature, under mechanical milling.¹⁶⁹ Spectroscopic and microscopic analyses indicated the introduction of multiple hydroxyl groups on the sidewalls of CNTs. This wet-mechanical procedure resulted in water-soluble and shortened CNTs after milling, while CNTs with optimized aspect ratio were obtained by adjusting the ball milling parameters. Another ball milling method was also reported, taking place in the presence of ammonium bicarbonate, and allowing the introduction of amino- and amido-functional groups on the surface of CNTs. Eventually, the as-prepared functionalized CNTs were effectively disentangled and shortened.¹⁷⁰

3. Noncovalent Interactions

In this section of the Review, we survey from a chemical perspective noncovalent interactions of CNTs with molecular species, particularly emphasizing the mechanism of the nanotube–molecule interaction, the colloidal stability of the adducts, and their functional properties. In this frame, noncovalent interplay between CNTs and organic materials is particularly attractive because of the possibility of decorating the CNTs surface, without disturbing their characteristic π system, with various groups.^{4c} In the past few years, the noncovalent surface treatment of CNTs by surfactants or macromolecules was widely used in the preparation of both aqueous and organic solutions, to obtain highly stable suspensions of individually dispersed nanotubes. A detailed discussion on the noncovalent modification of CNT sidewalls by a variety of chemical species is presented in the following paragraphs.

3.1. Polynuclear Aromatic Compounds

Condensed aromatic derivatives carrying a hydrophilic or hydrophobic moiety can dissolve CNTs in aqueous and organic media, respectively. Nakashima and co-workers¹⁷¹ studied the solubilization of CNTs in aqueous environment with phenyl, naphthalene, phenanthrene, and pyrene-ammonium amphiphiles. The authors described the importance of π – π interactions between the aromatic moieties and the CNT sidewalls, because phenyl and naphthalene-based amphiphiles were not able to disperse CNTs in water. On the contrary, the pyrene derivative was a much more efficient solubilizer as compared to the phenanthrene one. Near-IR photoluminescence measurements revealed that the aqueous SWCNTs/pyrene-ammonium suspension possesses a specific range of diameters of the carbon nanostructures (0.89–1.00 nm). Moreover, Prato and co-workers¹⁷² immobilized anionic porphyrins onto the soluble CNT/pyrene-ammonium hybrid, by electrostatic interactions, to yield electron donor–acceptor nanohybrids (Figure 13). A series of photochemical experiments confirmed that long-lived radical ion pairs were formed as a result of a rapid excited-state deactivation of the porphyrin chromophores. In an analogous approach, the alkyl-ammonium entity of CNT/pyrene-ammonium hybrid was utilized to complex a crown ether-modified fullerene.¹⁷³ Steady-state and time-resolved fluorescence studies revealed efficient quenching of the singlet excited state of C₆₀ in the nanohybrids. Further studies involving nanosecond transient absorption measurements confirmed electron transfer to be the quenching mechanism, in which the fullerene anion radical was spectroscopically identified.

Concerning the use of nonionic pyrene solubilizers, Harada and co-workers¹⁷⁴ studied the dispersion of SWCNT material with pyrene- β -cyclodextrin in aqueous medium. The solution of the CNT-based hybrid was stable for more than a month. Similarly, Bertozzi and co-workers¹⁷⁵ functionalized SWCNTs with pyrene-glycodendrimer derivatives, which gave permanent solubility in aqueous media. To evaluate their cytotoxicity, the authors cocultured glycodendrimer-coated SWCNTs with HEK293 cells. It was found that cells cultured with glycodendrimer-coated SWCNTs proliferated at the same rate as cells grown in the absence of CNT material. By contrast, unmodified SWCNTs greatly hampered the growth of HEK293 cells. In an analogous study, Francis and co-workers¹⁷⁶ solubilized pristine SWCNTs with α -pyrene- ω -aminooxypolyethyleneglycol (MW \approx 2000) in aqueous

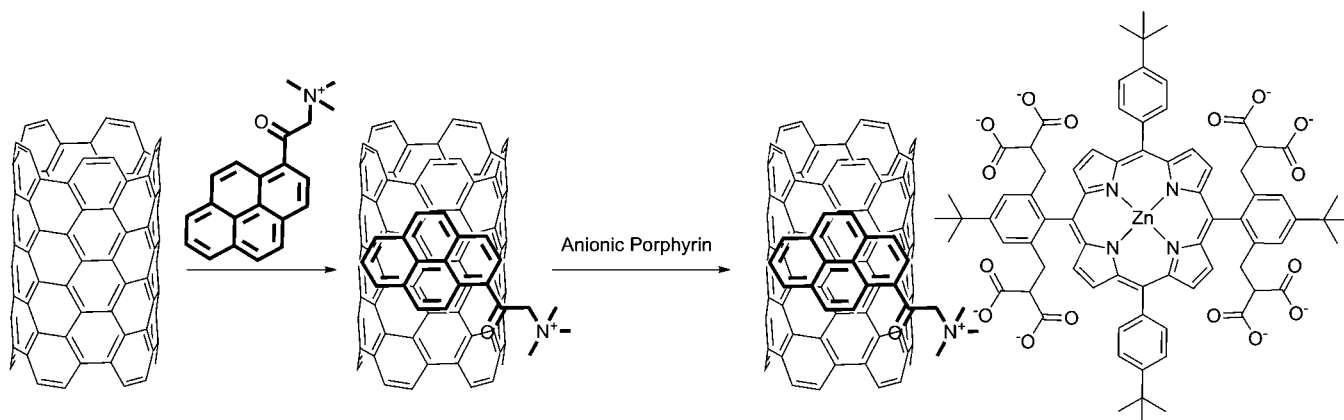


Figure 13. Noncovalent interactions of SWCNTs with anionic porphyrins through a pyrene linker.

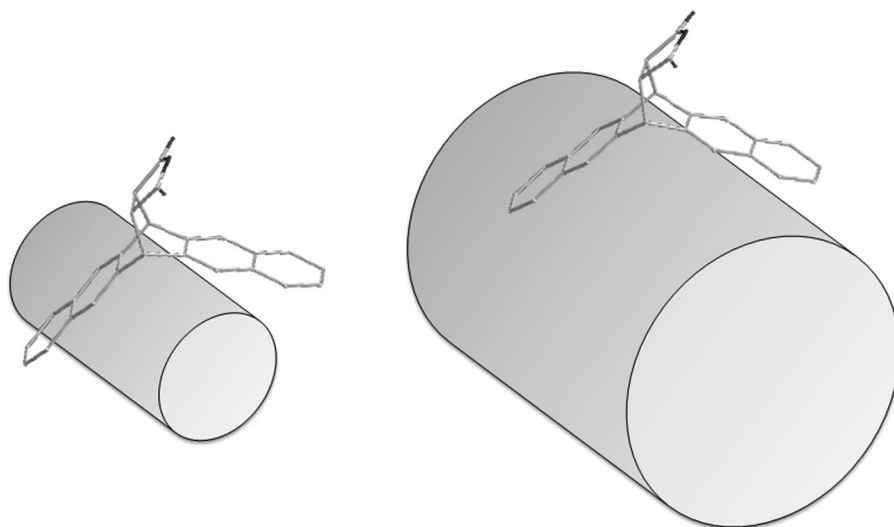


Figure 14. Schematic illustration of the interaction of a “tweezer” molecule with different diameter CNTs.

medium. These amino-terminated polymeric surfactants provided a convenient means to attach onto biomolecular platforms through well-defined chemical linkages. In the same context, SWCNTs were modified with pyrene and phospholipids, which are bound to different surfactant polymers based upon poly(γ -glutamic acid) and poly(maleic anhydride-*alt*-1-octadecene).¹⁷⁷ The as-prepared nanomaterials showed enhanced stability in aqueous solutions at different pH values, at elevated temperatures, and in serum and exhibited remarkably long blood circulation upon intravenous injection into mice, making them suitable for *in vivo* applications, including imaging and drug delivery. Finally, the noncovalent functionalization of SWNTs with pyrenecarboxylic acid afforded stable aqueous dispersions, providing an alternative to the frequently used oxidative acid treatment functionalization of carbon nanotubes.¹⁷⁸

Pyrene derivatives were also used to disperse CNTs in organic solvents. Representative examples of pyrene-linked functionalities include fullerene,¹⁷⁹ pyro-pheophorbide,¹⁸⁰ tetrathiafulvalene,¹⁸¹ hydroxypropyl cellulose,¹⁸² hydrolyzed poly(styrene-*co*-maleic anhydride),^{183a} and fluorenevinylene.^{183b} A series of photophysical measurements gave strong evidence about the through space interaction between CNT sidewalls and the pendant functionalities.

A novel strategy for diameter-selective separation of CNTs was developed by the Tromp group (Figure 14).¹⁸⁴ Separation was based on size-selective noncovalent matching of a pentacene Diels–Alder alkylated adduct to the sidewalls of

SWCNTs, enabling suspension of the CNTs in solvents in which they would otherwise be insoluble. The authors demonstrated size-selective solubilization of CNTs with diameter of about 1.15 nm, whereas larger diameters precipitated after centrifugation. CNT-based field-effect-transistors fabricated from these diameter-selected CNTs showed markedly improved electrical properties as compared to nonselected CNTs. In a similar approach, a modified diazapentacene derivative was shown to disperse CNTs in organic media under sonication.¹⁸⁵ The authors proposed that solely π – π interactions occur between the components.

Another class of species that were immobilized onto CNT sidewalls is light harvesting systems, such as porphyrin derivatives. Diederich and co-workers¹⁸⁶ studied the dispersibility of SWCNTs in the presence of fused porphyrin oligomers. When a trimer was used, a very stable, dark solution was obtained after sonication of the isolated residue for a little time. This solution remained stable upon standing indefinitely, with no sedimentation observed, even after centrifugation for 20 min at 5000 rpm. In sharp contrast, the fused dimer was not able to exfoliate the CNTs bundles in the acidified tetrahydrofuran solution. The strong supramolecular interaction between the components was investigated by UV–vis–NIR spectroscopy and AFM imaging. The authors observed remarkable shifts in the maxima of the porphyrin Soret bands, and this phenomenon was attributed to the complexation process. At the same time, the groups of Adronov¹⁸⁷ and Valentini¹⁸⁸ studied the

supramolecular complexation of CNTs with linear polymeric and dendritic porphyrins, respectively. Stable CNT suspensions were obtained even after centrifugation process in both systems. In the case of dendritic porphyrin systems, the authors did not observe any shift in the maxima of UV-vis-NIR spectra of neat porphyrin derivative and the complex.

3.2. Interactions with Other Substances

A simple and nondestructive method for nanotube solubilization is based on noncovalent interactions of amphiphilic molecules (surfactants) with nanotube surfaces: hydrophilic parts of such molecules interact with the solvent and hydrophobic parts are adsorbed onto the nanotube surface, thus solubilizing CNTs and preventing them from the aggregation into bundles and ropes. Typical examples include charged surfactants such as sodium dodecyl sulfate (SDS), tetraalkylammonium bromide, or cetyltrimethyl ammonium bromide (CTAB), as well as neutral surfactants, such as Triton. The individual solubilization of CNTs by various ionic and nonionic surfactants was extensively discussed and reviewed during recent years.¹⁸⁹

Room temperature ionic liquids and in particular the ones based on the alkyl-substituted imidazolium ion are amphiphilic substances and may be considered to be cationic surfactants. Depending on the counteranion, ionic liquids can be miscible with organic or aqueous media. In CNT chemistry, ionic liquids were used for the first time for the synthesis of a gel consisting of highly exfoliated bundles^{57,190} and subsequently as solvents for various chemical reactions.^{109a,191} In a similar approach, Hao and co-workers¹⁹² used ethylammonium nitrate ionic liquid to incorporate MWCNTs into a lyotropic hexagonal liquid crystal system, while Kocharova et al.¹⁹³ used 1-(12-mercaptododecyl)-3-methylimidazolium bromide, to produce thiolated SWCNTs, which could self-assemble on gold. More recently, it was reported the functionalization of SWCNTs with the insoluble-in-water hydroxyferriprotoporphyrin (hematin), in the presence of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) ionic liquid. The as-prepared hybrid material was used for the construction of a biosensor sensitive to trichloroacetic acid with good analytical performance and low detection limit.¹⁹⁴

A noncovalent approach for the dissolution and exfoliation of SWCNTs in water by a rigid, planar, and conjugated diazo dye, Congo red (CR), was reported by Hu et al.¹⁹⁵ Using a simple physical grinding treatment, the mixture of SWCNTs and CR could be dissolved in water with a solubility as high as 3.5 mg/mL. The complete elimination of free CR from the mixture hardly changed this excellent solubility. High-resolution transmission electron microscope images showed that the SWCNT bundles were efficiently exfoliated into individual tubes or small ropes. The π - π stacking interaction between adsorbed CR and SWCNT sidewalls was considered responsible for the high solubility.

Ogoshi and co-workers studied the supramolecular interaction and solubilization of SWCNTs in aqueous media with macrocyclic host molecules, such as cucurbiturils¹⁹⁶ (Figure 15a) and sulfonatocalixarenes (Figure 15b).¹⁹⁷ In the former case, the macrocycle was able to selectively solubilize nondefective SWCNTs in water. Thus, cucurbiturils can be used not only for CNT solubilization but also for purification of defective material. In the case of calixarenes, efficient exfoliation of CNT bundles in water took place due to

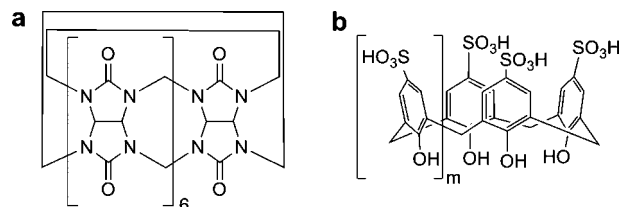


Figure 15. Water-soluble macrocyclic compounds used for the solubilization of CNTs: (a) cucurbit[7]uril and (b) calix[*m*]arenes where *m* = 3 or 6.

electrostatic repulsion forces. Upon addition of guest molecules in the CNT-macrocycle hybrid, aggregation of SWCNTs was observed due to the formation of host-guest complexes between the macrocycle and the guest.

Bourlinos and co-workers¹⁹⁸ reported a simple approach toward water-dispersible CNT-silica composites, where charged silica moieties provide the CNT solubilization. The hydrophobic surface of the pristine CNTs was wetted with vinylsilane molecules through noncovalent interactions between the vinyl groups and the aromatic walls of the nanotubes. Alkaline condensation of the impregnated silane led to bonded oligomeric siloxane species that after calcination afforded ultrafine silica nanoparticles with Si-O-Si cross-links. The as-obtained silica nanoparticles exhibited a high concentration of acidic surface silanols that upon alkaline treatment were readily converted to the corresponding anionic silanoxo groups. In this way, the silica sheath over nanotubes acquires a negative surface charge that offered the ensuing hybrid ionic character and hence dispersibility in water.

Bottini et al.¹⁹⁹ dispersed pristine SWCNTs in water by ultrasonication in the presence of mercaptopropyl trimethoxysilane. As revealed by the sharp features in the UV-vis spectra and by transmission electron microscopy, the collected centrifuged sample was composed of small bundles of nanotubes coated by a thin layer of organosilane molecules.

Another facile, solvent-free noncovalent method for the modification of SWCNTs by tertiary organic phosphines PR₃ (where R = Ph or C₈H₁₇) was described by Coleman and co-workers.²⁰⁰ The modified material showed enhanced exfoliation into common organic solvents. AFM analysis showed a significant debundling of the SWCNTs upon phosphine treatment. Interestingly, Raman spectroscopy and absorption spectroscopy in the near-infrared region indicated that the disruption of the intrinsic electronic structure of the nanotubes upon modification is minimal. XPS data obtained from the modified nanotubes suggested that the tertiary phosphines interact through charge transfer mechanism, presumably via the lone pair of electrons on the phosphorus with the “electron-deficient” nanotubes.

Ikeda and co-workers²⁰¹ studied the solubilization of SWCNTs in organic solvents through the formation of admixtures with barbituric acid (BA)/triaminopyrimidine (TP) complexes using mechanochemical high-speed vibration milling (HSVM) and sonication methods. In contrast, neither BA nor TP alone were capable of solubilizing SWCNTs. These results strongly suggested that the formation of a hydrogen-bonding network made possible the formation of multipoint interactions with the CNT sidewalls.

Lee and co-workers²⁰² studied the noncovalent modification and dispersion of CNTs in organic media by 3-hexylthiophene oligomers. The authors observed that an increase in the number of sulfur head groups improved the dispersity of SWCNTs, whereas the regioregularity of the oligomer

played an important role in dispersing tubes. Furthermore, Raman spectroscopy and XPS spectroscopy showed that the sulfur atom head groups enhance interactions between the thiophenes and the SWCNT walls. The analysis demonstrated that a well-designed thiophene oligomer (with 12 monomeric units) could afford well-dispersed SWCNT solutions with long-term dispersion stability (CNT concentration $\sim 0.1 \text{ g L}^{-1}$).

By using a simple chemical treatment, Windle and co-workers^{203a} effectively wetted and dispersed SWCNTs in saturated sodium hydroxide solutions of an alcohol–water mixture with little surface damage or shortening of the tubes. The treated material was soluble as individual tubes in many common organic solvents. It was considered that ethoxide ions easily diffused into the bundles, reducing the intertube forces. In a similar study, Li et al.^{203b} studied the noncovalent functionalization of CNTs by 2-aminoethanol in the presence of sodium hydroxide. Alkoxide ions were found to coat the CNT sidewalls, thus rendering the CNT material completely unbundled. The presence of amine groups was shown to improve the interfacial interaction of tubes with an epoxy-based matrix.

3.3. Interactions with Biomolecules

Ever since the discovery of CNTs, researchers have been exploring their interaction with various biomolecules to integrate the carbon nanostructures in biological applications.²⁰⁴ The recent expansion and availability of biofunctionalization methods made it possible to generate a new class of bioactive CNTs, which were conjugated with proteins, carbohydrates, or nucleic acids. The modification of a tube on a molecular level using biological molecules is essentially an example of the “bottom-up” fabrication principle of bionanotechnology. The availability of these biomodified CNT constructs opens up an entire new and exciting research direction in the field of chemical biology, finally aiming to target and to alter the cell’s behavior at the subcellular or molecular level.

An important class of biomolecules having high affinity with the CNTs sidewalls is proteins. They are natural polyampholytes containing both hydrophobic and hydrophilic domains, whereas their hydrophilicity depends on the amino acid sequence and pH conditions. A number of studies were reported concerning the sonication-assisted debundling and dispersion of CNT–protein hybrids in aqueous and/or polar media. These include high molecular weight natural proteins such as lysozyme,²⁰⁵ bovine serum albumin,^{205b,206} hydrophobins,²⁰⁷ as well as synthetic oligopeptides. The latter include reversible cyclic peptides,²⁰⁸ phenylalanine-based peptides,²⁰⁹ amphiphilic helical peptides,²¹⁰ cysteine-based peptides,²¹¹ silica-precipitating peptides,²¹² and porphyric peptides.²¹³

Matsuura et al.^{205b} investigated the mechanism by which sonication leads to dispersion in four different water-soluble protein solutions. The cyclic dichroism (CD) spectra of the hybrid dispersions showed that the proteins are partially unfolded when adsorbed onto CNT sidewalls. Thus, the behavior of CNT dispersion by water-soluble proteins was found to be related to their unfolding by heat denaturation and refolding process. In the papain and pepsin solutions, tubes were not dispersed probably due to very slight exposure of the inner hydrophobic domains as a result of insufficient changes in protein unfolding during the sonication process. In the lysozyme and bovine serum albumin solutions, however, the proteins were found to interact with the

sidewalls of “frayed” SWCNTs, because the inner hydrophobic domains of the partially unfolded proteins would be exposed in a more efficient mode.

Concerning the solubilization of CNTs with oligopeptides (molecular weight below 3000), Zorbas et al.²⁰⁹ examined a series of peptides that varied the number of phenylalanine moieties. Optical spectroscopy and AFM measurements revealed that sequences that placed more aromatic amino acids in certain positions were more effective at dispersing individual SWCNTs. Without aromatic amino acids in the sequence, it was found that only small bundles of SWCNTs could be suspended. CD spectra, correlated with AFM analyses, provided evidence of increased SWCNT dispersion with increasing aromatic residues in solution. Altogether, these data demonstrated that π – π stacking interactions between aromatic residues of a peptide and the graphitic surface of a SWCNT play an important role in peptide-based dispersion of tubes. In a similar study, Dieckmann and co-workers^{210a} enhanced appreciably the colloidal stability of CNT–oligopeptide complex in aqueous media by cross-linking the amino acid moieties with carbodiimide chemistry. CNT–protein hybrids received great interest in various fields of technology, such as templates for inorganic particle arrays^{207,212} or channels for field-effect transistor devices.²¹⁰

Another example of biomolecules assembled onto the CNT sidewalls involves the polysaccharides. In recent years, several groups reported that chitosan derivatives interact strongly with CNTs, forming stable hybrids that can be effectively dispersed in aqueous solutions.²¹⁴ Techniques used to study CNT–chitosan interactions include UV–vis, fluorescence, Raman, as well as electron microscopies. In an elegant work, Akins and co-workers^{214b} developed a simple, efficient process for the water dispersion and diameter-selective separation of SWCNTs, unlike the other reported approaches in which a repetitive dispersion–centrifugation process was required. Smaller-diameter SWCNTs were found to be preferentially dispersed and wrapped by chitosan in the aqueous supernatant part that resulted after noncentrifuged precipitation, while larger diameter tubes sedimented. Chitosan-modified SWCNTs were also tested for their singlet oxygen production upon a two-photon excitation as compared to nonfunctionalized SWCNTs and oxidized SWCNTs. The nanotube-mediated generation of singlet oxygen could find applications in both targeted destruction of tumor cells and selective degradation of drug molecules.^{214g}

Liu et al.²¹⁵ demonstrated that alginate acid (AA) can efficiently solubilize MWCNTs in aqueous solution. Furthermore, it was shown that the addition of alkaline-earth-metal, transition-metal, heavy-metal, and lanthanoid cations to the AA-wrapped nanotubes resulted in the precipitation of MWCNTs from aqueous solution, due to intertube bridging by complex formation. In a similar work, Wallace and co-workers²¹⁶ demonstrated the remarkable dispersive properties of hyaluronic acid (HA) for SWCNTs.

The integration of CNT–polysaccharide composites in biological applications was demonstrated by their successful utility as electrochemical sensors of glucose.²¹⁷ Using a different approach, Strano and co-workers²¹⁸ have fabricated an affinity sensor for glucose molecule, based on SWCNT photoluminescence. The authors prepared colloidally stable suspensions of dextran-coated CNT material by first covalently adding phenyl groups to dextran. Addition of a plant lectin induced nanotube aggregation and decreased CNT

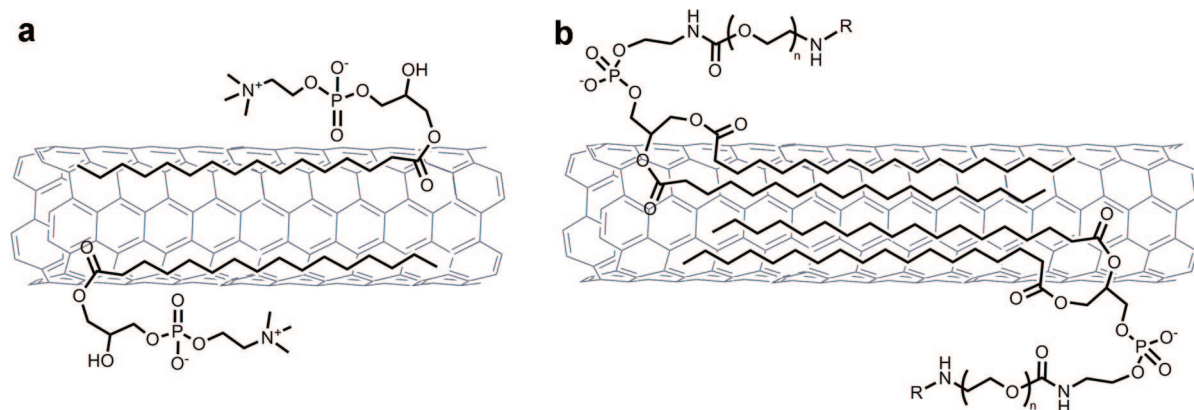


Figure 16. Decoration of SWCNTs with (a) single-tailed phospholipids terminated with trimethylammonium moiety and (b) double-tailed phospholipids terminated with polyethyleneglycol ($n = 45$) chains ($R =$ folic acid or fluorescein).

fluorescence, whereas subsequent additions of glucose broke apart the aggregates, resulting in a restoration of CNT emission.

In another approach, the binding of oligonucleotide-encapsulated SWCNTs with platinum-based DNA cross-linkers, such as potassium tetrachloroplatinate and cisplatin, was reported by Hersam and co-workers.²¹⁹ Following cross-linking, the platinum salt adduct was reduced, thus decorating the DNA-encapsulated SWCNTs with platinum nanoparticles. In this procedure, DNA chains served as both noncovalent dispersant for SWCNTs in aqueous solution and a binding substrate for platinum compounds and nanoparticles. In the field of molecular recognition for sensing applications, the groups of Johnson²²⁰ and Lee²²¹ independently demonstrated a versatile class of nanoscale chemical sensors based on single-stranded DNA as the chemical recognition site and SWCNT field effect transistors as the electronic read-out component. These devices were shown to respond to gas organic odors or proteins, causing a detectable conductivity change.

Bertozi and co-workers²²² described a biomimetic surface modification of CNTs using *N*-acetylgalactosamine-linked polymers designed to mimic natural glycoproteins, called mucins. The latter coat the surfaces of numerous cell types and present epitopes for receptor-mediated cell–cell recognition. To enable noncovalent adsorption of the glycopolymer, an octadecyl (C18) aliphatic chain was introduced on one end of the chain. CNTs modified with mucin analogues were soluble in water and were found to bind to cell surfaces via specific carbohydrate receptors. Whereas unmodified CNTs induced cell death, the functionalized CNTs were found to be nontoxic.

To make CNTs soluble in aqueous media, researchers explored the possibility of decorating the graphitic surface with phospholipid derivatives. Recent works demonstrated that lysoglycerophospholipids (single-tailed phospholipids) terminated with a short trimethylammonium moiety (Figure 16a) offer unprecedented solubility for SWCNTs, while double-tailed glycerophospholipids were found ineffective in rendering SWCNTs soluble.²²³ Using transmission electron microscopy (TEM), the authors showed that lysophospholipids wrap SWCNTs as striations whose size and regularity are affected by the polarity of the lysophospholipids. At the same time, the Dai group developed an analogous noncovalent approach for modifying the surface of short SWCNTs (average length ~ 200 nm) with more polar double-tailed phospholipids terminated with polyethyleneglycol or dextran chains (Figure 16b).^{224–228} These functionalized tubes were

utilized as transporters of various biological moieties inside cells through an endocytosis mechanism. The transporting capabilities of CNTs combined with suitable functionalization chemistry lead to novel nanomaterials with applications in fields such as selective destruction of cancer cells by near-infrared radiation,²²⁴ gene therapy by RNA transport,²²⁵ tumor targeting by recognition through an oligopeptide,²²⁶ drug delivery,²²⁷ and near-infrared fluorescent tags for selective probing of cell surface receptors and cell imaging.²²⁸ In most cases, noncovalently biofunctionalized CNTs exhibit longer blood circulation and relatively low uptake in the reticuloendothelial system,²²⁹ as compared to covalently biomodified CNTs.^{92–94}

4. Endohedral Filling

From a chemist's perspective, one of the most fascinating properties of CNTs is their ability to encapsulate molecules and confine them to form quasi-1D arrays.^{189b,230} Many reports on molecule-filled CNTs concentrated on the physical properties of the nanotubes and their response to the presence of the absorbed molecules inside their empty cavity.

4.1. Encapsulation of Fullerenes

During the 1990s, research was first devoted to filling multi- and single-walled CNT material by C_{60} and higher fullerenes, producing peapod structures (Figure 17a).^{189b,230} The fullerene-filled nanotubes have been characterized by various spectroscopies, and their optical-electronic transport properties have been studied in detail.²³¹ In addition, peapod structures have been successfully suspended in aqueous media by using a pyrene ammonium surfactant.²³²

Kawasaki et al.²³³ investigated the structural behavior of C_{60} -SWCNT peapods under high pressure up to 25 GPa by in situ synchrotron X-ray diffraction measurements. It was observed that the C_{60} – C_{60} distance in a carbon nanotube decreases with pressure from 0.956 nm at 0.1 MPa down to 0.845 nm at 25 GPa. It was also found that the distance value upon complete release of the pressure after compression remained at a value lower than its initial value. These experimental results indicated that pressure induced the polymerization of C_{60} molecules inside the CNT cavity.

The efficiency of C_{60} release from the cavity of SWCNTs by solution-phase treatment was investigated independently by the groups of Simon²³⁴ and Yudasaka.²³⁵ X-ray diffraction and Raman spectroscopy showed that fullerenes could be removed from the inside of large diameter SWCNTs

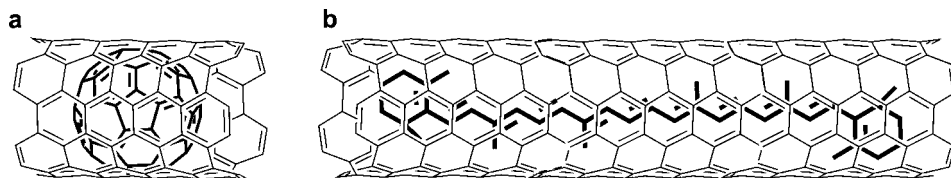


Figure 17. Illustrative images of SWCNTs encapsulated with (a) C_{60} and (b) β -carotene.

($d > 1.5$ nm) with a high efficiency using dichlorobenzene as a solvent.²³⁴ The latter medium effectively removed weakly bound C_{60} from the inner cavity of the tubes, which was explained by the high solubility of C_{60} in dichlorobenzene. Through transmission electron microscopy, it was found that the efficiency of C_{60} release from large diameter SWCNTs (1.5–7.0 nm) in toluene was maximized in the ones having diameter between 3 and 5 nm.²³⁵ The difficulty of C_{60} release from SWCNTs with diameters of 5–6 nm was explained by the effective packing of C_{60} inside those tubes.

Not only was pristine C_{60} inserted into the cavity of SWCNTs, but also some modified spheres such as azafullerene,²³⁶ exohedrally modified C_{60} ,²³⁷ fullerene-based salts (CsC_{60}),²³⁸ and endohedral metallofullerenes ($Er_3N@C_{80}$).²³⁹ The conditions used for the preparation of these peapod structures mainly include sublimation, solution-based treatment, and/or insertion under supercritical CO_2 atmosphere.

Using HRTEM, it was demonstrated^{237a} that the presence of long aliphatic groups attached exohedrally to fullerene cages significantly increases the mean intermolecular distances of the trapped species. Comparison of alkyl groups of different length demonstrated that bulkier spacers provide larger interfullerene separations. This indicates the possibility to control the position and the density of molecules in SWCNTs, and therefore tune the electronic properties of these hybrid systems.

Using a sophisticated technique, Suenaga and co-workers²³⁹ demonstrated the orientational changes of C_{80} and $Er_3N@C_{80}$ inside SWCNTs by aberration-corrected TEM imaging. A detailed structure of the peapod structures was identified at real atomic level resolution.

Concerning the filling of double-walled carbon nanotubes (DWCNTs), the pioneering study of Khlobystov and co-workers²⁴⁰ showed that different crystalline phases of C_{60} can be formed within the empty cavity. The structure of the encapsulated C_{60} crystal was defined by the internal diameter of the DWCNTs, as the molecules adjusted their packing arrangement to maximize van der Waals interactions. The authors also showed that fullerenes in $C_{60}@DWCNTs$ interact with the outer layer of DWCNTs, as demonstrated by the efficient filling of DWCNT material with internal diameters of less than 1.2 nm. The strong interaction of tubes having smaller internal diameters with the fullerenes was supported by Raman scattering studies.²⁴¹ Thermogravimetric analysis of such peapod structures demonstrates that their thermal stability was greatly enhanced as compared to pristine DWCNTs (by about 55 °C).²⁴²

4.2. Encapsulation of Organic Substances

Besides fullerenes, other systems introduced in the cavity of CNTs include organic molecules, inserted most often by sublimation and solution-based conditions. Fujita and co-workers²⁴³ demonstrated the doping of perylene-3,4,9,10-tetracarboxylic anhydride (PTCDA) into the cavity of SWCNTs. TEM images showed the existence of one-

dimensionally arranged PTCDA molecules in the tube, whereas heat treatment at high temperature in a vacuum of these PTCDA-filled SWCNTs induced new Raman signals ranging between 300 and 400 cm^{-1} , which were assigned to the radial breathing mode of vibration associated with the newly formed inner tubes.

Kataura and co-workers studied the encapsulation of conjugated dyes, such as carotene²⁴⁴ (Figure 17b) and squarylium,²⁴⁵ into the cavities of SWCNTs. Photoluminescence spectra revealed excited energy transfer from the trapped molecules to the SWCNTs.

In an analogous work, the confinement of an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) into the inner cavity of MWCNT material was studied by Wu and co-workers.²⁴⁶ Electron diffraction patterns and differential scanning calorimetry spectra indicated the formation of ionic crystals in the confined space. Whereas the melting point of pure ionic liquid was about 6 °C, the crystal formed inside the MWCNTs possesses an unexpectedly high thermal stability (mp \sim 220 °C).

Another class of substances immobilized into the cavity of CNTs is polymeric species, such as polystyrene,²⁴⁷ poly(*n*-vinylcarbazole),²⁴⁸ polypyrrole,²⁴⁸ polyacetylene,²⁴⁹ and $C_{10}H_2$ polyyne.²⁵⁰ In most cases, the filling of the CNT interiors was accomplished by in situ polymerization process with the aid of supercritical CO_2 . The CNT–polymer hybrids were fully characterized by Raman, TGA, FTIR, XRD, and TEM spectroscopies.

4.3. Encapsulation of Inorganic Substances

Whereas encapsulation of iodide salts (KI, CsI, PbI_2) into MW- and SWCNTs was already demonstrated by the group of Green in Oxford, the same group extended their studies in the case of DWCNTs.²⁵¹ The composites were prepared using a melt-phase filling procedure. The imaging and subsequent structural analysis of the encapsulated metal iodide crystals was performed with a combination of phase restored high-resolution transmission electron microscopy technique, structural modeling, image simulation, and X-ray powder diffraction measurements. The atomically resolved structures of the inorganic crystals were seen to contain several lattice defects including interstitials and vacancies as well as distortions of the crystal planes. By using a different protocol, soaking of ultra short SWCNTs into a $GdCl_3$ aqueous solution, Wilson and co-workers²⁵² reported the confinement of aquated Gd^{3+} ion clusters within the inner cavity of tubes. Because of the large magnetic moment of the ions, these species showed a 40–90 times enhancement of magnetic resonance imaging efficacy when compared to any Gd^{3+} -based contrast agent in clinical use.

In analogous works, cage-like ions or molecules were successfully inserted into the cavities of SW- and/or DWCNTs. These include charged polyoxometalates, such as phosphotungstic acid ($H_3PW_{12}O_{40}$)²⁵³ and Linqvist ion (W_6O_{19}),²⁵⁴ as well as neutral oligosilasesquioxanes ($H_8Si_8O_{12}$).²⁵⁵ Phosphotungstic acid peapods were shown to be stabilized

effectively in aqueous media due to electrostatic repulsion forces.²⁵³ The interaction between the graphitic sidewalls and the encapsulated species was examined by FTIR and Raman spectroscopies, whereas their direct imaging was performed by HRTEM.

By using a very sophisticated imaging technique, electron tomography (3D TEM), Ersen et al.²⁵⁶ characterized the morphology and location of palladium nanoparticles inside the cavity of MWCNTs. The palladium salt precursor was first sucked inside the nanotube channel by means of capillarity force, and then reduction of the salt took place in hydrogen atmosphere at 400 °C. Three-dimensional TEM analysis revealed that introduction of foreign elements inside the tube channel was strongly influenced by the diameter of the tube inner channel; that is, easy filling seemed to occur with a tube channel ≥ 30 nm, whereas with tubes having a smaller channel (< 15 nm), almost no filling by capillarity occurred, leading to the deposition of the metal particles only on the outer wall of the tube.

A very significant approach to fabricate metal nanowires inside the cavity of SWCNTs by a nanotemplate reaction was reported by the groups of Shinohara²⁵⁷ and Kataura.²⁵⁸ Thermal annealing of SWCNTs filled with endohedral Gd-based metallofullerenes²⁵⁷ or ferrocene²⁵⁸ resulted in the formation of various metal nanowires, including a single metal atom chain, a one-dimensional alignment of metal atom squares, and nanowires that correspond to a one-dimensional segment of the bulk close-packed structure. Direct measurements of the interatomic distance using HRTEM images showed that the Gd–Gd distance is 0.41 nm, which is larger than the bond length of the bulk Gd crystals.²⁵⁷ It was suggested that charge transfer between encapsulated Gd atoms and the CNT plays a crucial role in stabilizing the observed Gd nanowire structures with large Gd–Gd distances. The structural properties of such ultrathin Gd nanowires encapsulated in SWCNTs were recently confirmed by density functional calculations.²⁵⁹

5. Decoration of CNTs with Metal Nanoparticles

Metal nanoparticles can be immobilized onto the skeleton of CNTs by a variety of diverse techniques.²⁶⁰ The preparation of CNTs/metal nanoparticles hybrid materials is an important research area as the new hybrid materials generated possess unique properties and are potentially useful for nanotechnological applications. In principle, the efficient decoration of CNTs with metal nanoparticles is accomplished via (i) covalent linkage, (ii) electrodeposition as well as electroless deposition, and (iii) noncovalent interactions. The different strategies for the preparation of CNTs/metal nanoparticle materials are highlighted in the following subsections in the form of examples adapted from the recent literature.

5.1. Covalent Linkage

Thiol-modified CNTs produced either by (i) the thermal solvent-free modification of MWCNTs with aliphatic dithiols or aminothiols,²⁶¹ or by (ii) reaction of MWCNTs with 4-thiolphenyl diazonium salts,²⁶² or by (iii) photolysis of cyclic disulfides with SWCNTs²⁶³ were used as substrates for the assembly of gold and palladium nanoparticles on the skeleton of CNTs. In addition, thiol-functionalized MWCNTs, prepared by the reaction of 4-aminothiophenol with acyl chloride-modified MWCNTs, were used for the immobilization of platinum nanoparticles with high loading.²⁶⁴ The latter

were fabricated by a liquid-phase borohydride reduction of chloroplatinic acid. The CNT–Pt hybrid material showed enhanced electrocatalytic activity in methanol oxidation and oxygen reduction reactions. Moreover, gold nanoparticles were immobilized onto the surface of thiol-functionalized MWCNTs without any agglomeration after the reduction of gold(III) chloride by γ -irradiation²⁶⁵ (Figure 18).

Jerome and co-workers²⁶⁶ used the inexpensive and commercially available 4,4'-azobis(4-cyanovaleric acid) to modify MWCNTs by a traditional radical addition mechanism via thermolysis. This procedure released carboxylate groups, which serve as grafting points for magnetite nanoparticles (Fe_3O_4). In a similar way, an azoalkynitrile was used as a radical initiator to produce alkylcyano-modified MWCNTs, which were subsequently hydrolyzed to release carboxylates.²⁶⁷ Silica coated magnetite nanoparticles of average size 60 nm and modified with an amino terminal group were combined with the carboxylated MWCNTs via an amidation reaction. The as-prepared hybrid material was further used for the rapid separation of aromatic compounds in water.

5.2. Direct Formation on Defect Sites

The decoration of acid purified and ammonia treated MWCNTs by single crystal zinc oxide nanoparticles was investigated as a function of temperature. Briefly, MWCNTs were continuously coated by zinc oxide nanoparticles having an average size up to 48 nm, when treated at temperatures as high as 600 °C. However, the thin layer of zinc oxide on the surface of MWCNTs became discontinuous when the temperature of heat treatment reached 750 °C.²⁶⁸ Acid-purified SWCNTs were also used as scaffolds for the deposition of zinc oxide nanoparticles, which upon excitation with the UV light underwent charge separation and injected electrons in the nanotube skeleton.²⁶⁹ More recently, atomic layer deposition, which is a special modification of chemical vapor deposition for the development of thin films, was used for the growth and the direct deposition of zinc oxide nanoparticles on defect sites of the SWCNT sidewalls. Zinc oxide nanoparticles were formed by using diethyl zinc and water as precursors, without any annealing.²⁷⁰ In addition, if an amorphous aluminum oxide shell was used as intermediate layer covering the SWCNT surface, the final morphology of the ZnO nanocrystals became smooth and controllable.²⁷¹

Nanocomposite materials consisting of Pd nanoparticles deposited on aligned MWCNTs were fabricated through hydrogen reduction of palladium- β -diketone precursor in supercritical CO_2 processing.²⁷² By changing the concentration of palladium- β -diketone, the loading density of metallic nanoparticles on the nanotubes was shown to be tailored appreciably.

A low temperature, microwave-induced synthesis of a high-purity silicon carbide (SiC)–SWCNT composite was reported by Mitra and co-workers.²⁷³ The reaction, which was completed within 10 min, involved the decomposition of chlorotrimethylsilane and the nucleation of SiC spheres directly on the SWCNT bundles.

5.3. Electroless Deposition

Dai and Qu²⁷⁴ developed an electroless deposition method for the decoration of CNTs with a large variety of metal nanoparticles, by supporting the CNTs on a metal substrate

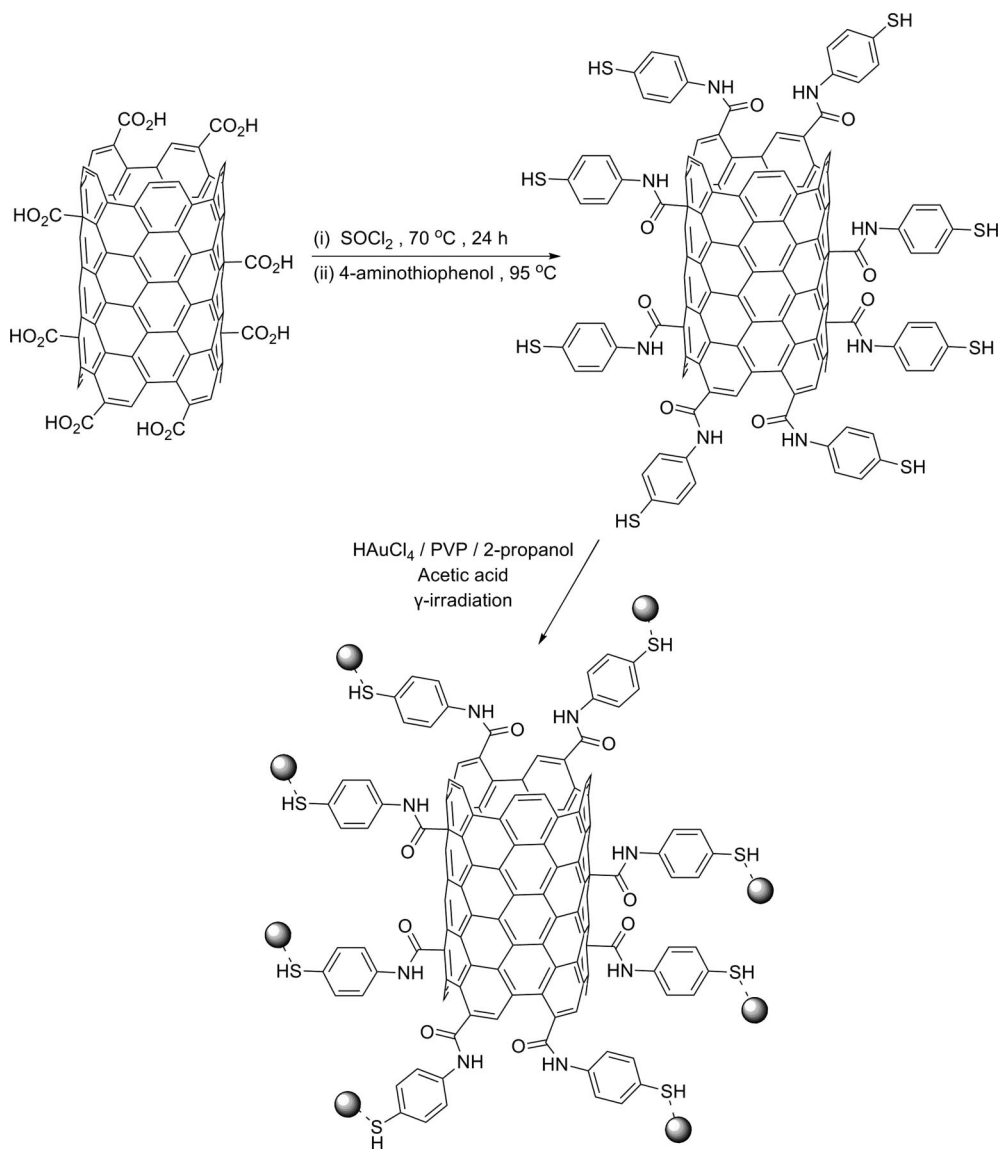


Figure 18. Immobilization of gold nanoparticles onto thiol-functionalized CNTs.

with a lower redox potential than that of the metal ion to be reduced into nanoparticles, without using any reducing agent. By this method, the deposition of metal nanoparticles was achieved via the redox reaction of a galvanic cell, in which the CNTs act as a cathode for metal deposition (i.e., gold, palladium, or platinum) from the reduction of metal ions in solution, while metal atoms (like silver or copper) are oxidized to the corresponding ions and dissolved in solution. Furthermore, the same research group proposed the shape- and size-controlled syntheses of platinum and gold nanoparticles by reaction of the appropriate aqueous solutions with a copper foil via a galvanic displacement reaction at different metal ion concentrations and/or reaction times.²⁷⁵

5.4. Electrodeposition

Palladium nanoparticles were electrochemically dispersed on SWCNTs by electroreduction of octahedral palladium(IV) complex formed on the SWCNT surface through a three-step procedure.²⁷⁶ First, a SWCNT paste electrode was fabricated and electrochemically activated by introducing carbonyl and carboxylated groups at defect sites of the nanotubes. Next, an octahedral complex of palladium(IV)

was formed on the SWCNT surface from the electrochemical reduction of a palladium salt. Similarly, an electrochemical reduction approach was developed to produce aligned CNT arrays uniformly decorated by platinum nanoparticles.²⁷⁷

Gold nanoparticles were electrodeposited on the sidewalls of SWCNTs, which were already functionalized with the amine-terminated ionic liquid 1-ethylamine-2,3-dimethylimidazolium bromide. Self-assembly of this amine to the gold nanoparticles led to a new nanocomposite, which can be used as scaffold for the glucose oxidase, thus allowing its direct electrochemistry.²⁷⁸

A simple controllable method is reported by Haram and co-workers²⁷⁹ for the filling and coating of oxidatively shortened and -COOH-functionalized MWCNTs with silver. This was achieved through anodic dissolution of a silver electrode in the presence of an aqueous dispersion of modified MWCNTs. The composition of silver-MWCNTs hybrids was controlled by the concentration of the oxidized MWCNTs dispersion and current, voltage, and time of the electrophoresis procedure. In a recent study, Kern and co-workers²⁸⁰ demonstrated that the functionalization of individual SWCNTs from aqueous solutions of Prussian Blue

dye by electrodeposition left the metallic tubes unaffected, whereas semiconducting tubes were strongly p-doped. The field of electrodeposition of several metal nanoparticles on SWCNT surface for various applications such as catalysis and sensing was reviewed recently.²⁸¹

5.5. Chemical Decoration

A very facile method for the decoration of CNTs with metal nanoparticles comes from the reduction of a metal salt in the presence of a surfactant. It is well-known that CNTs form colloidal dispersions in organic solvents or water via adsorption of a surfactant onto their sidewalls. In many cases, the surfactant also keeps the role of the reducing agent of the metal salt for the formation of metal nanoparticles. In that context, gold, platinum, and ruthenium nanoparticles were formed on SWCNTs or MWCNTs sidewalls by a mild reduction of the corresponding metal salts using polyethylene glycol as both reducing agent and surfactant.²⁸² The addition of several ionic substances, such as sodium dodecyl sulfate (SDS), sodium *p*-toluene sulfonate, lithium trifluoromethanesulfonate, or lithium perchlorate, facilitated the reduction of chloroplatinic acid in ethylene glycol solutions and resulted in high dispersions and high loadings of platinum nanoparticles on CNTs without aggregation.²⁸³ Similarly, SDS-modified MWCNTs were heavily covered by monodispersed ruthenium nanoparticles via thermal reduction reaction of ruthenium chloride in the presence of ethylene glycol,²⁸⁴ while erbium nanoparticles were deposited onto oxidized-MWNTs by the same process using the corresponding erbium salt.²⁸⁵

In another work, the self-regulated reduction of platinum and palladium salts in the presence of SDS micelles of CNTs, without the presence of any other reducing agent, led to the deposition of platinum and palladium nanoparticles on CNTs surfaces.²⁸⁶ The as-prepared materials showed enhanced solubility in polar organic solvents and great catalytic activity in hydrogenation reactions of olefinic bonds and the formation of carbon–carbon bond reactions.

The cationic CTAB is another surfactant that serves as a positively charged template for the homogeneous adsorption of the anionic polyelectrolyte poly(sodium 4-styrenesulfonate), thereby ensuring high-density coverage of negative charges on the surfaces of CNTs. This negatively charged hybrid material was employed as a precursor for the efficient adsorption of Fe³⁺ ions via electrostatic attraction, and then the assembly of Fe₃O₄ magnetic nanoparticles along CNTs sidewalls was carried out by a polyol-medium solvothermal method.²⁸⁷

Cha et al.²⁸⁸ prepared MWCNT–Co composites from the reduction of cobalt(II) acetoacetonate by 1,2-hexadecanediol in a MWCNT/dioctylether/oleylamine dispersion. This hybrid material was screen-printed and sintered to produce a nanocomposite emitter, which exhibits a low turn-on electric field and produces a high current density.

In a similar way, Park et al.²⁸⁹ reported the in situ preparation and deposition of copper disulfide nanocrystals onto MWCNT surfaces. The morphology of the copper disulfide nanocrystals was varied from spherical particles (average size 4 nm) to triangular plates (average size 12 nm) by increasing the concentration of the precursors. These nanomaterials were used to construct devices, which show a remarkable performance for applications involving both solar cells and electrochemical glucose sensors.

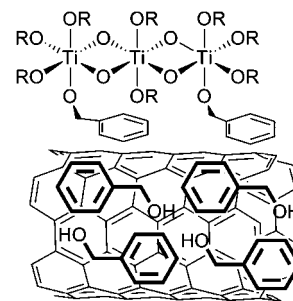


Figure 19. Decoration of SWCNTs with TiO₂ in the presence of benzyl alcohol.

In another procedure, gold nanoparticles were deposited on the sidewalls of MWCNTs by the self-catalyzed reduction of gold salts either in the presence of surfactants²⁹⁰ or without any surfactants in aqueous solutions,²⁹¹ while in the same context, a novel nanocomposite in which CNTs were decorated with both gold nanoparticles and a conducting polymer, such as polythiophene, was prepared.²⁹² In a different approach, in situ decoration of MWCNTs with gold nanoparticles via a microwave-assisted ethylene glycol reduction reaction of gold salts was reported by Raghuvver et al.²⁹³ Microwave-assisted treatment of MWCNTs resulted in the introduction of carboxyl, carbonyl, hydroxyl, and allyl moieties onto their sidewalls, which acted as preferred nucleation points for reducing gold ions from solution.

Dendrimer-modified CNTs were used as substrates for the stabilization of metal and metal oxide nanoparticles, as well as quantum dots. In the first step, acyl chloride MWCNTs were covalently functionalized by amine-terminated PAM-AM dendrimers via an amidation reaction. The as-prepared nanohybrids were used as anchors for the in situ preparation and stabilization of gold, copper, silver, and platinum nanoparticles, via reduction of the corresponding metal precursor by sodium borohydride.²⁹⁴ In addition, silicon oxide and titanium oxide nanoparticles were directly grown onto dendrimer modified MWCNTs by hydrolysis of tetraethyl orthosilicate or titanium tetraisopropoxide in water.²⁹⁵ These nanomaterials showed enhanced water dispersibility. Finally, cadmium sulfide quantum dots (average size 1.4 nm) were formed and stabilized onto SWCNTs, which were covalently modified with an amino polyester dendrimer. These hybrids exhibited reduced fluorescence emission intensity as compared to that of cadmium sulfide quantum dots anchored on untethered dendrimers, due to partial emission quenching by the SWCNTs.²⁹⁶

Titanium oxide nanoparticles were also deposited on the sidewalls of SWCNTs in the presence of benzyl alcohol, which acted as a surfactant.²⁹⁷ The concentration of benzyl alcohol in the reaction mixture affected the morphology of the inorganic oxide coating, and a molar ratio benzyl alcohol: titanium 5:1 showed the best results. One possible conformation of two benzyl alcohol molecules with a 6-fold coordinated titanium complex on the SWCNT surface was suggested by the authors as shown in Figure 19.

Wang and co-workers reported the preparation of CNTs homogeneously coated with a silica layer, via a simple combination of sol–gel chemistry and sonication. This hybrid material was used, with the aid of an amine interlinker, as a scaffold for the loading of several metal nanoparticles such as gold and platinum nanoparticles as long as hybrid nanoparticles as gold/platinum and gold/silver nanoparticles. These new materials were successfully em-

ployed for the fabrication of electrochemical devices with high performance.²⁹⁸

Wet impregnation is another procedure that was used for the fabrication of CNTs–metal nanoparticles hybrid materials. In this context, when SWCNTs were immersed in ethanolic aqueous palladium or platinum salts solutions, the spontaneous formation of metal nanoparticles on the side walls of SWCNTs was observed.²⁹⁹ A variation of that method for the deposition of silver, gold, palladium, and platinum nanoparticles onto SWCNTs and MWCNTs was presented by Han and co-workers.³⁰⁰ Moreover, when a dispersion of CNTs in an organic solvent such as *N,N*-dimethylformamide, toluene, or acetone was added in a biphasic mixture of a freshly prepared aqueous solution of the metal salt and diethylether, a thin film of metal–CNTs composite was formed at the aqueous/organic interface.

In a different approach, platinum metallization of SWCNT–single-stranded DNA conjugates proved to be an effective method to modulate the conductivity of these nanomaterials.³⁰¹ In particular, acid-treated SWCNTs were modified by single stranded-DNA via an amidation reaction, while in a second phase, a two-step chemical reduction and deposition of platinum colloids was followed. The as-prepared nanomaterial exhibited negative differential resistance, which indicated a probable biomimetic route to the fabrication of resonant tunneling diodes.

5.6. Deposition of Nanoparticles onto CNTs

Alkylthiol-derivatized gold nanoparticles were deposited onto sidewalls of SWCNTs and MWCNTs in a dichloromethane suspension.³⁰² Except for the hydrophobic interaction between the alkyl chains of the capping/linking molecules and the hydrophobic backbones of the nanotubes, an alternative strategy in the direct assembly simultaneously included the specific interaction between Au nanoparticles and the nitrogen atoms of bamboo-like CNTs as proposed by Zhu and co-workers.³⁰³

In a different approach, platinum nanoparticles prepared in ethylene glycol were modified by triphenylphosphine and deposited on the surface of MWCNTs, preserving their small size (~2 nm).³⁰⁴ The prepared Pt/CNT composite materials showed higher electrocatalytic activity in methanol oxidation than the commercial catalyst. In an alternative approach, acid-treated MWCNTs were used for the deposition of platinum nanoparticles with average diameter 4 nm using a sonochemical treatment method.³⁰⁵ Similarly, oxidized CNTs by hydrogen peroxide treatment were used as substrates for the stabilization of silver and gold nanoparticles, which were produced by using resorcinol as a reducing agent via a sonochemical method.³⁰⁶

Finally, the fabrication of a tunable hybrid photodetector with a responsivity as high as 5 orders of magnitude, upon the deposition of derivatized dodecanoic acid, monodispersed, crystalline zinc oxide nanoparticles of 6 nm diameter, onto the surface of pristine SWCNTs, was proposed. Importantly, due to the photoinduced adsorption and desorption of oxygen from the nanoparticle surface, the resulting devices showed important photoswitching effects. The different photosensitivities of zinc oxide nanoparticles to different wavelengthed light resulted in the fine-tunability of the conductance in the devices by different UV light.³⁰⁷

5.7. π – π Stacking and Electrostatic Interactions

Another approach for the preparation of metal nanoparticles–CNTs hybrid materials relies on the noncovalent modification of CNTs with bifunctional molecules, which act as interlinkers between the nanotube surface and the nanoparticles. These molecules contain mostly aryl or polyaromatic moieties on the one terminal, which interact noncovalently with the six-membered carbon rings of the nanotubes, and amino, carboxyl, or thiol groups on the other terminal, which allow them to adsorb different nanoparticle precursors via electrostatic interactions, followed by the in situ formation of the corresponding nanoparticles on the nanotubes. In particular, several pyrenyl analogues³⁰⁸ and aryl thiols³⁰⁹ were used as interlinkers for the decoration of CNTs with platinum, gold, silver, cadmium sulfide, and silica nanoparticles or silica gel nanobeads.

In another case, a cationic polyelectrolyte, polyethyleneimine,³¹⁰ was used to modify acid-purified MWCNTs through both the electrostatic interaction between negatively charged MWCNTs and polyethyleneimine and the physisorption process, analogous to polymer wrapping. Polyethyleneimine was found to act simultaneously as an adsorbing center and a reducing agent for AuClO_4^- salt, resulting in a MWCNT–gold heterogeneous composite material. In the same way, hexagonal zinc sulfide nanocrystals were prepared and covered the sidewalls of polyethyleneimine-modified MWCNTs resulting to hybrid composites. Interestingly, the latter showed a slight blue shift in the UV–visible spectrum because of the quantum size effect of the attached zinc sulfide on the wall of MWCNTs.³¹¹

To avoid the structural damage of CNTs surface from the oxidation procedure, Chen and co-workers proposed a mild functionalization treatment based on the free radical polymerization of the ionic liquid monomer 3-ethyl-1-vinylimidazolium tetrafluoroborate. In such a way, an ionic liquid polymer on the CNT surface was formed.³¹² This process allowed the introduction of a large number of surface functional groups on the CNTs with uniform distribution to anchor and grow Pt and PtRu nanoparticles with a diameter distribution between 0.9 and 2.4 nm. The as-prepared nanohybrid materials showed an excellent performance in the direct electrooxidation of methanol and seem to be a promising catalyst support in fuel cells.

On the basis of interactions of electrostatic nature, Dong and co-workers³¹³ developed a reproducible, noncovalent strategy to functionalize MWCNTs via embedding tubes in polysiloxane shells. (3-Aminopropyl)triethoxysilane molecules adsorbed to the nanotube surfaces via hydrophobic interactions were polymerized simply by acid catalysis and formed a thin polysiloxane layer. On the basis of the embedded MWCNTs, negatively charged gold nanoparticles were anchored to the nanotube surfaces via electrostatic interactions between the protonated amino groups and the gold nanoparticles. Furthermore, these gold nanoparticles could further grow and magnify along the nanotubes through heating in HAuCl_4 aqueous solution at 100 °C; as a result, these nanoparticles were joined to form continuous gold nanowires with MWCNTs acting as templates. Similarly, Yang and co-workers³¹⁴ attached positively charged Pt nanocubes by surfactant adsorption onto polystyrenesulfonate-wrapped CNTs. Moreover, the Pt nanocube/CNT composites exhibited excellent electrocatalytic activities toward oxygen reduction, which is of considerable importance for polymer

electrolyte fuel cells (PEFCs), batteries, and numerous other applications.

In another example, calcium carbonate, which is the major mineral component of the exoskeletons of many animals and has a good biocompatibility, was used as a component in mineral–CNTs composites for biomedical applications. Liu and co-workers³¹⁵ produced CNTs coated with calcium carbonate nanoparticles by precipitating CaCO₃ in the presence of MWCNTs, via a simple wet-chemical route, while Li and Gao³¹⁶ proposed that carboxy-functionalized MWCNTs and SWCNTs nucleate and stabilize micrometer-scale spherical crystals of vaterite, which is the least thermodynamically stable crystalline phase of CaCO₃. On the other hand, calcite, which is the most thermodynamically stable phase of CaCO₃ at room temperature, was prepared by diffusion of ammonium carbonate vapor into calcium chloride solution and decorated the sidewalls of CNTs.³¹⁷ In the case of pristine CNTs, rhombohedral calcite was obtained, while poly(isoprene-*b*-acrylic acid)-modified CNTs induced the formation of spherical or ellipsoidal inorganic particles consisting of calcite nanocrystals.

The mineralization of covalently modified SWCNTs with hydroxyapatite (HA) has been reported by Haddon and co-workers.³¹⁸ SWCNTs were functionalized with carboxylic, phosphonate, or sulfonic groups, and HA was crystallized on the surface of SWCNTs in solution phase and on thin films. In a similar way, MWCNT material, modified with carboxylic groups, has been used as a scaffold for the deposition of nanohydroxyapatite (nHA). The carboxylic groups on the surface acted as the coordination bonds for chelation of calcium in HA crystals.³¹⁹

Finally, the supramolecular self-assembly of several amphiphiles on the sidewalls of CNTs was used for the anchoring of palladium nanoparticles on the CNTs in aqueous media.³²⁰ These molecules contain a long alkyl chain for interaction with the nanotube surface and a polar head made of either nitrilotriacetic acid or pyridinium, for the binding of the nanoparticles. In the same way, an amphiphilic gadolinium(III) chelate was synthesized from commercially available stearic acid and adsorbed on MWCNTs. The resulting aqueous suspensions were stable for several days and examined as contrast agents to magnetic resonance imaging (MRI) applications.³²¹

6. Concluding Remarks

The overwhelming message conveyed through this Review is that the field of chemical functionalization of CNTs continues to grow steadily. As the attention of scientists, in recent days, is focused on technological applications, the excitement in this field arises from the versatility of the CNT material as well as the possibility to create new and novel material architectures with unique properties. The production of CNTs has become easier and cheaper by the years, and the quality of as-prepared CNTs has improved as far as the contaminated impurities such as amorphous carbon or metal catalysts are concerned. Thus, the major challenge for the near future is the development of improved methods for the production of CNTs with uniform sizes in both lengths and diameters and especially the chirality, which is mainly responsible for their outstanding physical properties. Without a doubt, CNTs bridge the gap between the molecular realm and the macro-world.

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