Introducing functional groups onto the surface of carbon nanotubes helps to solubilize these useful molecules and facilitates their study.

Soluble Carbon Nanotubes

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Abstract: Carbon nanotubes have attracted great interdisciplinary interest because of their unique structure and properties. However, carbon-nanotube research is challenged by several problems, such as: i) mass production of material, ii) control of length, diameter, and chirality, and iii) manipulation for use in diverse technological fields. Issues regarding the synthesis and purification as well as the functionalization and solubilization of carbon nanotubes are relevant topics in this rapidly growing field. In this paper, covalent and noncovalent approaches to functionalized and solubilized nanotubes are examined in detail, with particular emphasis on the change of properties that accompany the chemical modification.

Keywords: composites · functional materials · nanostructures · nanotechnology · nanotubes

Introduction

The discovery of carbon nanotubes (CN)[1] and the prospect of developing novel carbon-based nanomaterials has excited worldwide interest among researchers.[2] Following the enthusiastic scientific response, CNs have quickly been proven to possess unique electronic, mechanical, and structural properties.[3]

However, the inherently difficult handling of CNs poses serious obstacles to their further development. Essentially, dissolution of CNs may be necessary for proper chemical and physical examination and use. The ability to solubilize and separate discrete CN molecules from the tight bundles they form would not only open new avenues in the field of nanotechnology, but would also aid in their purification, eventually allowing easier manipulation.

Several excellent reviews dealing with the many aspects of the chemistry of CNs have already appeared in the litera-

ture.[4–7] Herein, we focus on recent developments in the area of soluble CNs, with an eye to the use of these materials in diverse technological applications.

Synthesis and Purification of Pristine Nanotubes

There are two main types of CN with high structural perfection: single-walled nanotubes (SWNTs), which consist of a single graphite sheet seamlessly wrapped into a cylindrical tube, and multiwalled nanotubes (MWNTs), which comprise an array of concentric cylinders. SWNTs and MWNTs are usually produced by arc-discharge,[8] laser ablation,[9] chemical vapor deposition (CVD),[10] or gas-phase catalytic process (HiPco) methods.[11]

Most frequently, the diameter of CNs varies roughly between 0.4 nm and 3 nm for SWNTs and from 1.4 nm to 100 nm for MWNTs.[12] Up to now, all currently known production methods generate CNs with impurities. In general, such impurities consist of carbon-coated metal catalysts (which, e.g., contaminate HiPco-produced nanotubes) and both carbon-coated metal and carbon nanoparticles/amorphous carbon (in arc-discharge-produced nanotubes). Also, structural defects, such as dangling bonds, are often found in most types of CN. The main techniques applied for purification of CNs are oxidation of contaminants,[13] flocculation and selective sedimentation,[14] filtration,[15] size-exclusion chromatography,[16] selective interaction with organic polymers,[17] or microwave irradiation.[18] However, considerable problems remain for most of the present purification techniques. Some of these methods rely on the difference in resistance to oxidation, either thermal or chemical, between CNs and impurities. Since this difference is often marginal, significant quantities of CN are destroyed or altered before all impurities are removed. Alternatively, nondestructive methods such as microfiltration or size-exclusion chromatography can be employed, but tend to be slow and inefficient processes. An easy way for purifying HiPco nanotubes, based on the treatment of raw CNs in a domestic microwave oven under air in the absence of any solvent, has been recently reported by our group.[18b] Thus, the contaminant metallic nanoparticles are oxidized and, in a second step, washed away with concentrated hydrochloric acid.

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Applications of Carbon Nanotubes

Among the plethora of applications that have been envisioned for CNs, polymer composites, field-effect transistors, field-emission displays, and hydrogen storage appear to be the most promising areas. For example, CNs have been considered to be novel components for molecular electronics and for integration into conventional circuits.[19]

The extraordinary structural and mechanical properties of CNs make them ideal candidates for incorporation into new families of composite materials. Interestingly, CN–polymer composites, could be tougher and more scratch-resistant than any other materials.[2b, 20] However, the development of such hybrids meets some serious obstacles, as CNs tend to phase segregate. In fact, CNs do not spontaneously suspend in polymers, so that the chemistry and physics of dispersion will play a crucial role. The research challenge is particularly arduous: due to strong attractive interactions, nanotubes aggregate to form bundles or "ropes" of up to tens of nanometers in diameter for SWNTs, which are very difficult to disrupt. Furthermore, these ropes are tangled with one another like spaghetti. With high shear, these ropes can be untangled, but it is extremely difficult to further disperse them at the single-tube level. However, this limitation can be overcome by introducing various functional groups on the CN surface that can help dispersion in the composite material.

Recently, CNs have been used as field-emission electron sources.[21] This technology finds applications in the construction of flat panel displays and X-rays to microwave generators.[22]

Finally, storage of hydrogen on CNs could represent a great development on fuel-cells and a milestone toward energy-clean systems. However, despite the exciting potential and the progress made so far, the results are controversial. For example, there have been many reports claiming high and efficient hydrogen storage on CNs that, however, have often been disputed.[23, 24] The highest hydrogen storage capacity on SWNTs exceeds 10 wt% and the smallest values approach zero with the main reason for these discrepancies being the differences in CN sample quality (e.g. production method, purification, handling, etc).

Dissolution of Nanotubes in Organic Solvents

Over the years, a systematic effort has been applied, aimed at finding appropriate media to solubilize pristine nanotubes. SWNTs typically exist as ropes or bundles of 10–30 nm in diameter because of strong van der Waals interactions that result in stacking and entangling. Although it is possible to wet the SWNT raw material in hot nitric acid,[13a] shortened CNs (with an average length less than 500 nm) are obtained in this manner because of the harsh conditions used.

At the early stages, most studies focussed on dissolution of laser-oven-produced SWNTs (diameter ca. 1.2 nm). Highly polar solvents such as N,N-dimethylformamide (DMF), N-methylpyrrolidinone, and hexamethylphosphoramide (HMPA) were the most attractive choices for dispersion of

SWNTs.[25] Furthermore, stable suspensions of SWNTs were prepared by sonicating purified material in DMF.[26] In addition, purified SWNTs obtained by oxidation[13a] were found to dissolve in aromatic amines ($\sim$8 mg mL^{-1} in aniline).[27] The latter phenomenon was explained by the formation of charge-transfer complexes between amine solvent molecules and SWNTs.

The solubility of small-diameter HiPco-SWNTs was also studied in several organic solvents, and 1,2-dichlorobenzene was found to be the most appropriate medium by UV/vis absorption spectroscopy.[28]

The final conclusion is that the dispersion of CNs in a specific medium depends strongly on the method used for their growth, the content of impurities, and the procedure applied for purifying these materials.

Solubilization by Noncovalent Interactions

This type of solubilization is particularly attractive because of the possibility of attaching various groups without disturbing the π system of the graphene sheets. It has been shown that CNs can be solubilized in aqueous media in the presence of amphiphilic molecules (surfactants).[15, 16] The hydrophobic part is oriented toward the surface of the carbon nanotubes, whereas the polar moiety interacts in the outer region with solvent molecules.

Recently, noncovalent anchoring of aromatic molecules to the side-walls of SWNTs has been achieved. A molecule containing a planar pyrene moiety that could adsorb to the surface of CNs through strong π–π stacking interactions was utilized as the anchor (Scheme 1).
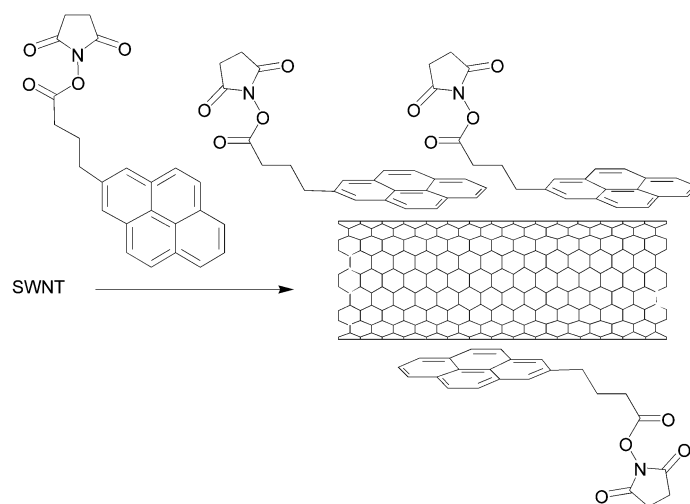
Scheme 1.

The pyrene moiety was specifically designed in such a way that a variety of molecules with intriguing properties could be further coupled via amide linkages.[29] Thus, for example, immobilization of proteins, DNA, and other smaller biomolecules on the side-walls of SWNTs was achieved. Importantly, this methodology has the potential to couple the electronic properties of CNs with the specific recognition properties of

the immobilized biomolecules and ultimately lead to the construction of miniaturized sensors. Similarly, pyrene-carrying ammonium ions were used to help solubilize CNs in water.[30]

In a different approach for the noncovalent functionalization of CNs, bundles of SWNTs helically wrapped with a conjugated polymer were synthesized.[17b] In the initial experiments, SWNTs were added to a solution of poly-(m-phenyl-enevinylene) substituted with octyloxy alkyl chains, and a stable suspension of CNs was obtained upon sonication. Physicochemical studies of this SWNTs–polymer complex revealed that the polymer wraps itself around the SWNTs as a result of π–π stacking interactions. Stilbenoid polymers have been used extensively in this kind of functionalization because of their well-defined dimensions.[31] In a similar approach, it was shown that soluble nanotube–polymer composites can be prepared by in situ polymerization of phenylacetylene.[32a] In the above cases, the composites formed are soluble in organic solvents such as chloroform, toluene etc.; however, polymer wrapping around nanotubes has also taken place in aqueous media. The association of nanotubes with linear polymers like polyvinyl pyrrolidone and polystyrene sulfonate in water has been studied.[32b] CNs were found to unwrap on changing the medium to less polar solvents.

Short rigid conjugated polymers, such as poly(arylene ethynylene)s, have also been used as solubilizing agents: the polymers being attached by a nonwrapping approach onto the CN while some pendant alkyl groups contribute to the solubility.[33] As in the case of pyrene-carrying surfactant, the major interaction is stacking by van der Waals forces. By using the nonwrapping approach, SWNTs can be solubilized in organic solvents (chloroform) by simply mixing them with polymers.

In order to exploit the unique properties of CNs in a biological setting, SWNTs were dispersed in aqueous solutions of amylose.[34] In the presence of iodine, which causes preorganization of amylose from its linear conformation to a helical one, very stable and soluble nanotube–amylose composites were found to form. When the starch–CN material was examined by atomic force microscopy (AFM), small bundles of CNs covered with amorphous polysaccharide were visualized. Importantly, addition of amyloglucosidase (an enzyme that hydrolyzes starch), to the otherwise stable starch–CN solution, led to the precipitation of CNs; this suggests a new method for purifying CNs.

Functionalized Carbon Nanotubes

The chemical modification of CNs is an emerging area in materials science. Among the various approaches, the most general include: i) esterification or amidation of oxidized nanotubes, ii) side-wall covalent attachment of functional groups.

Functionalization of oxidized nanotubes: One of the purification methods of raw CN material is based on oxidation in acidic media.[13a] Under these conditions, the end caps of the CN are opened, and acidic functionalities suitable for further derivatization are formed at these defect sites and at the side walls. Thus, long-chain alkylamines were condensed with the carboxylic groups present on the surface of the CN (Scheme 2).[7, 35] Activation of the carboxyl moieties with thionyl chloride and subsequent reaction with amines was preferred, or alternatively, direct condensation of oxidized nanotubes with amines.[36] In the latter case, the solubility of modified nanotubes was about 0.5 mg mL^{-1} in solvents like tetrahydrofuran or dichlorobenzene.
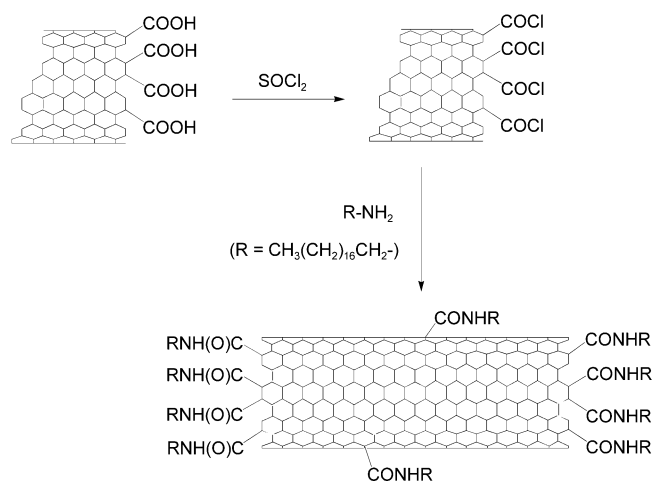
Scheme 2.

Not surprisingly, numerous amidation or esterification reactions to oxidized CNs that result in soluble functionalized materials have been reported.[37, 38] The electronic properties of such functionalized CNs remain intact, but in most cases the length of nanotubes is shortened.[13a]

As TEM images revealed, exfoliation of individual CNs from large ropes has been achieved during the functionalization process. This is extremely important as it allows easy characterization of the soluble CNs and facilitates their manipulation. Thus, recently, SWNTs functionalized in this manner have been purified by HPLC.[39] The presence of the functional addends at the defect sites of oxidized CNs has been mainly monitored by IR spectroscopy, which allows an easy identification of the amide- or ester-bond formation.

One of the most interesting examples of such functionalization involves the coupling of oxidized SWNTs with an alkyl thiol on gold nanoparticles.[13a, 40] The ultimate prospect of this type of material is for the construction of microelectrode arrays. Then, the potential applications of CNs could be expanded to the fields of bio-electrochemical sensors and designing novel molecular-recognition electrodes.

Covalent side-wall functionalization: The first report of this kind of approach involved treatment of SWNTs with dichlorocarbene. The transient species for this type of functionalization were generated by classical methods for carbene generation: i) chloroform–sodium hydroxide interaction[41] or ii) phenyl(bromodichloromethyl)mercury.[35] At the same time, SWNTs have also been found to react when treated with molecular fluorine at temperatures between 150 and 600 °C.[42] Depending on the reaction temperature, a different

degree of fluorination can be accomplished. Treatment of such derivatized CNs with hydrazine results in defunctionalization, so that intact CNs can be recovered. This type of functionalized nanotube dissolves well in alcohols,[43] although the fluorine atoms can be further substituted by alkyl groups to achieve better dissolution.[26a] However, when fluorination was applied to small-diameter HiPco-SWNTs, the nanotubes were cut to an average length of less than 50 nm.[44]

Recently, an extensive study of organic reactions leading to side wall functionalization of SWNTs, was performed.[5, 45] These reactions, already successfully applied to fullerenes, include: i) addition of nitrenes, ii) addition of carbenes, and iii) addition of radicals. To this end, alkyl azides were used as precursor compounds of nitrenes, and the resulting functionalized SWNTs were found to be soluble in dimethyl sulfoxide (DMSO). In the functionalization of SWNTs through carbenes, a dipyridyl imidazolium system was utilized and was found to link to the surface of nanotubes. Finally, perfluoroalkyl radicals were found to photochemically add on the side walls of SWNTs (Scheme 3).
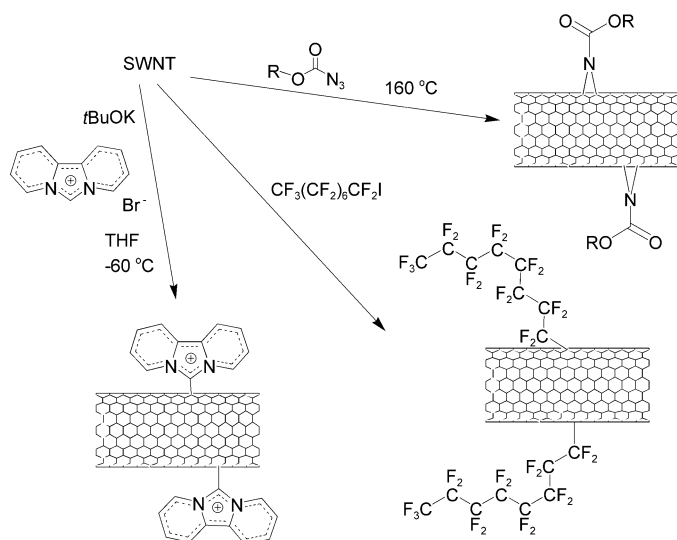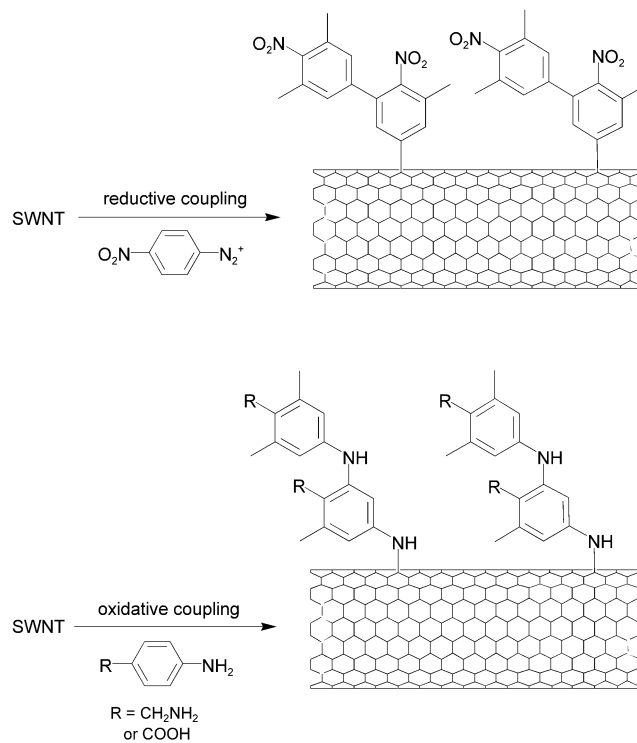

Scheme 4.

Scheme 5.

Scheme 3.

In another approach for covalent side-wall functionalization of CNs, aryl diazonium chemistry was performed.[6, 46] First, derivatization of HiPco-CN was achieved by electrochemical reduction of a variety of diazonium salts (Scheme 4).[46a] The solubility of these modified nanotubes was estimated to be 0.05 mg mL^{-1} in tetrahydrofuran. Subsequently, diazonium compounds chemically generated in situ were also reported.[46b,c] In addition to the electrochemically reductive coupling of aryl diazonium salts to CNs that resulted in C–C-bond formation, oxidative coupling of aromatic amines resulted in the attachment of amines directly to the surface of nanotubes (Scheme 5).[47]
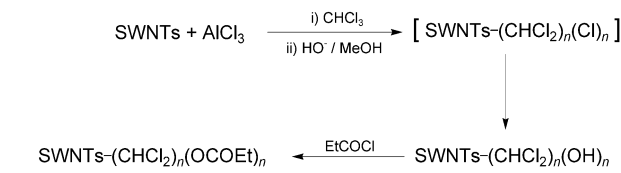
An electrophilic addition to HiPco-SWNTs was recently reported.[48] Upon mechanochemical reaction in the presence of a Lewis acid, such as aluminum trichloride (AlCl$_3$), a molecule of chloroform was found to add to the side walls of CNs (Scheme 6). It was also possible to exchange the chlorine
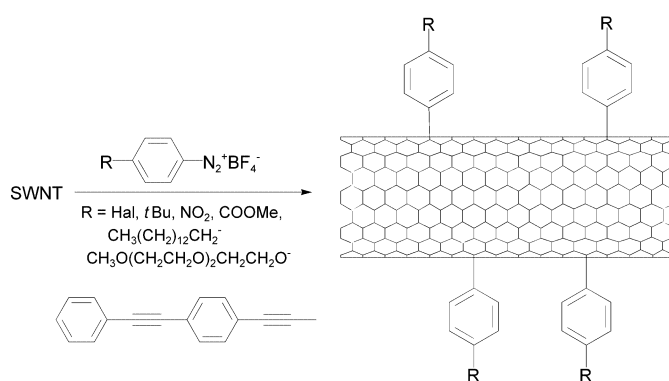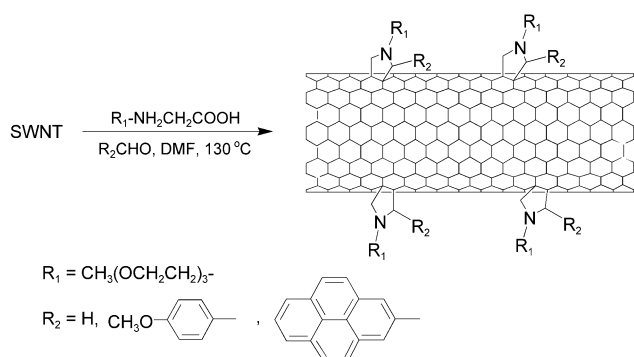

Scheme 6.

atoms with hydroxyl groups, which in a second step, were esterified to yield the corresponding esters.

This functionalization of HiPco-SWNTs not only resulted in soluble functionalized material but also showed that specifically derivatized CNs bearing free functional groups on their skeleton can serve as suitable synthons for the multistep synthesis of CN-based materials.

Based on the powerful methodology of 1,3-dipolar cycloaddition of azomethine ylides that has already met a broad acceptance in the fullerene field,[49] our group has developed a similar strategy for functionalizing and solubilizing CNs.[50, 51]

The main advantage of this reaction is the easy attachment of pyrrolidine rings substituted with chemical functions to the side walls of the CN, which can lead to the construction of novel materials with diverse applications. Thus, functionalized aldehydes can lead to 2-substituted pyrrolidine moieties located on the side walls of CNs, while modified α-amino acids could also lead to numerous diverse functionalized materials. The most successful approach for the in situ generation of azomethine ylides is based on the decarboxylation of immonium salts derived from condensation of α-amino acids with aldehydes.

Thus, when the 1,3-dipolar cycloaddition of azomethine ylides was applied to different types of CN (e.g. oxidized, HiPco-SWNTs, MWNTs), the reaction was found to be very effective.[50] In the first experiments, the triethylene glycol group was chosen as the N-substituent group of the α-amino acid due to its high solubilizing power (Scheme 7). Functionalized CNs were obtained as brown solids and found to be
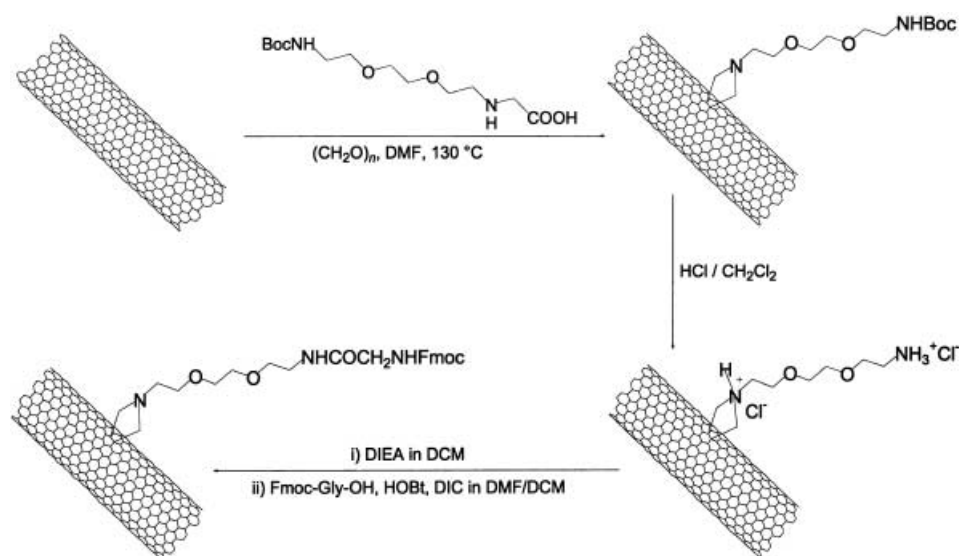

Scheme 7.

soluble in chlorinated solvents, acetone, and alcohols but insoluble in diethyl ether or hexane. It is worth mentioning that the solubility of such functionalized SWNTs in dichloromethane or chloroform was about 50 mg mL^{-1}. The degree of functionalization was estimated at about one pyrrolidine ring per one hundred carbon atoms of the CN. This high level of functionalization explains the high solubility and the change in color from black to brown of the CN. The covalent attachment of the pyrrolidine rings to the CN surface was clearly indicated when using HiPco-CN. These CNs show characteristic NIR bands, the so-called van Hove transitions, which disappear in the functionalized CNs.[50]

Having in hand such a powerful technique, we focused on the preparation of water-soluble functionalized CNs.[51] Among the scientific community there is great interest in

developing CNs as nanoscale biosensors.[29, 52] Research in this exciting area is not in full bloom yet, partly due to the difficulty of preparing water-soluble CN materials. Thus, under standard experimental conditions as described previously, when N-substituted α-aminoacid with a terminated amino $tert$-butoxycarbonyl (Boc) protected group[53] and $para$-formaldehyde were used as reagents for the functionalization of both SWNTs and MWNTs, the expected functionalized CNs were obtained (Scheme 8). Upon treatment with gaseous hydrochloric acid, deprotection of the masked N-Boc groups was achieved, and the corresponding ammonium salts were released. The resulting functionalized CNs possess a remarkably high solubility in water.

The synthesis and applications of fullerene amino acids and peptides have been already studied extensively.[54] In the case of ammonium-modified CNs, it was shown that they could be easily derivatized with N-protected amino acids.[51] Indeed, functionalization with N-protected glycine was achieved, which can be considered as the first step toward the synthesis of peptide-based CN materials (Scheme 8).

As mentioned previously, samples of raw CN include impurities such as amorphous carbon or metal nanoparticles. A new method for the purification of HiPco CNs has been recently developed in our laboratories; it consists of the following steps: i) organic functionalization of pristine nanotubes, ii) purification of the soluble adducts, iii) recovery of the starting material by thermal detachment of functional groups.[55] Combination of these steps led to high-purity material. The first step is based on chemical modification by 1,3-dipolar cycloaddition onto the surface of nanotubes. This chemical route results in solubilization of the functionalized nanotubes leaving the metal particles insoluble in the solvent used (DMF). Yet amorphous carbon was still present since it is soluble in the reaction medium. To further purify the functionalized nanotubes, a process consisting of dissolution and slow precipitation by using a combination of chloroform/diethyl ether was employed. The purified material was treated thermally at temperatures reaching 350 °C under an inert atmosphere. After this procedure, a weight loss of about 25 –

Scheme 8.

30 % of material was observed; this corresponds to the removal of the functional groups from the CN surface. The resulting solid was annealed at 900 °C and found to be insoluble in any solvent, while TEM images showed that CNs were recovered and, most importantly, were found to be free from impurities.[55]

Analytical Characterization and Visualization of Functionalized CNs

In general, it is very difficult to prove experimentally that covalent bonds are actually formed at the surface of the carbon framework of the tubes. Standard techniques in organic chemistry, such as proton or carbon NMR are complicated by the presence of several different isomeric forms. However, the solubilization of CNs provides opportunities for the spectroscopic characterization of these unique structures. Solution-phase absorption spectroscopy offers useful information about electronic transitions of CNs.[56] In general, UV/vis–NIR absorption spectra of functionalized CNs show a broad band around 250 nm, whose intensity decreases while reaching the near-infrared region. The spectra are basically featureless; this means that some of the electronic properties may have been lost because of extensive functionalization.[46a, 50] However, linear scattering arising from the big size of the functionalized CNs could lead to loss of resolution, thus making the attributions more complicated. HiPco-SWNTs have characteristic transitions in the NIR region that are partly[46] or totally[55] suppressed after functionalization.

Proton nuclear magnetic resonance spectroscopy is a very important tool for the structural assignment of organic and inorganic substances. However, proton signals appear to be broad as a result of the statistical distribution of the addends on the CN surface. Furthermore, interactions between the protons of the addends and the π system of the CN, as well as the restricted mobility of CNs in solution due to their large size, contribute to line-broadened signals.

Raman spectroscopy is an extremely useful tool for characterizing CNs.[57] Pristine CNs exhibit two main characteristic absorptions: the diameter-dependent radial breathing mode (RBM) below 350 cm^{-1} and the higher-frequency tangential mode at 1550–1600 cm^{-1}. In addition, functionalized CNs may show an increase in the so-called disorder mode at 1250–1450 cm^{-1}, but its relative intensity may depend on the laser excitation frequency.[58, 59]

Thermal gravimetric analysis (TGA) gives information on the purity[60] and also about functionalized CNs because the covalent attachments can be thermally eliminated.[46, 55] Moreover, microscopy techniques such as TEM (transmission electron microscopy), SEM (scanning electron microscopy), and AFM (atomic force microscopy) offer much insight into the presence of CNs in solution. Thus, in such a way, CN samples can be monitored qualitatively, and evidence about dimensions, purity, and aggregation can be obtained. In order to observe species attached to the surface of CNs, high-resolution instrumentation is required.

Conclusion

Research on carbon nanotubes has opened new avenues in materials science such that great opportunities for applications in nanotechnology are offered. Fundamental issues have been addressed and need to be resolved in order to get a wider approach to the nature of these unique structures. Nevertheless, it seems to be a question of how and when nanotechnology will be built on the advances made for carbon nanotubes rather than whether carbon nanotubes are useful materials with novel properties and promising applications.

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