Review

Chemistry of Carbon Nanotubes

Tong Lin,[A] *Vardhan Bajpai,*[A] *Tao Ji*[A] *and Liming Dai*[A,B]

[A] Laboratory of Functional Polymers and Carbon Nanomaterials, Department of Polymer Engineering,
   University of Akron, Akron OH 44325-0301, USA.

[B] Author to whom correspondence should be addressed (e-mail: ldai@uakron.edu).

Judicious application of site-selective reactions to non-aligned and aligned carbon nanotubes has opened a rich field of carbon nanotube chemistry. In order to meet specific requirements demanded by particular applications (e.g. bio-compatibility for nanotube biosensors and interfacial strength for blending with polymers), chemical modification of carbon nanotubes is essential. The tips of carbon nanotubes are more reactive than their sidewalls, allowing a variety of chemical reagents to be attached at the nanotube tips. Recently, some interesting reactions have also been devised for chemical modification of both the inner and outer nanotube walls, though the seamless arrangement of hexagon rings renders the sidewalls relatively unreactive. This review provides a brief summary of very recent progress in the research on chemistry of carbon nanotubes.

Introduction

Since their discovery by Iijima in 1991, carbon nanotubes have received considerable attention. These elongated tubular macromolecules, consisting of carbon hexagons arranged in a concentric manner with both ends normally capped by fullerene-like structures, can be seen as a graphite sheet rolled into a nanoscale tubular form (single-wall carbon nanotubes, SWNTs) or with additional graphene tubes around the core of a SWNT (multi-wall carbon nanotubes, MWNTs). Carbon nanotubes can be metallic or semi-conductive, depending on their diameters and arrangement of hexagon rings along the tube length. Apart from the interesting electronic characteristics, carbon nanotubes exhibit excellent mechanical and thermal properties. These interesting physicochemical properties make carbon nanotubes very attractive as electron emitters in field emission displays, reinforcement fillers in nanocomposite materials, scanning probe microscopy tips, actuators and sensors, as well as molecular-scale components in micro- or nano-electronic devices. However, it is difficult to synthesize carbon nanotubes with the surface characteristics demanded for specific applications (e.g. strongly interfacing with polymers in nanocomposites, or good biocompatibility for nanotube sensors). Therefore, surface modification and interfacial engineering are essential in making advanced carbon nanotubes of good bulk and surface properties.

Due to the seamless arrangement of hexagon rings without any dangling bonds, carbon nanotube walls are rather unreactive. Like C_{60} fullerene, the fullerene-like tips of nanotubes are known to be more reactive than the cylindrical nanotube walls,[1] and hence certain reagents can more readily react with the tips. However, this does not impact significantly on the chemistry of nanotubes as a whole due to the relatively small proportion of the tips in the structure. Although research on the chemical modification of carbon nanotubes is still in its infancy, some interesting work on carbon nanotube chemistry has recently been reported in literature. In this review, we will present an overview on carbon nanotube chemistry, covering both the covalent and non-covalent reactions at the tips, outerwalls, and innerwalls of SWNTs and MWNTs.

End Functionalization

Oxidation of Carbon Nanotubes

Early work on carbon nanotube chemistry can be traced back to the oxidation of carbon nanotubes at high temperature in air or oxygen.[1] Oxidation of carbon nanotubes at temperature above 700°C in the presence of air for 10 min resulted in the hemispherical end-caps opening, indicating that the hemispherical tips are more reactive than the graphite sidewall. This work also led to the prospect of filling foreign materials (e.g. metal oxide nanoparticles) into the hollow tubes.

The above mentioned early work on carbon nanotube chemistry was followed by gas-phase reactions with CO_2, N_2O, NO, NO_2, O_3, and ClO_2,[2] and amorphous carbon impurities are known to be more susceptible to gas-phase oxidation than carbon nanotubes. Solution-state chemical oxidation, however, was found to be more efficient for the purification and/or modification of carbon nanotubes. Since Tsang et al.[3] reported the liquid-phase oxidation of carbon nanotubes in HNO_3 in 1994, various oxidants have been shown to react with carbon nanotubes. Oxygen-containing acids, including HNO_3,[4–6] $HNO_3 + H_2SO_4$,[7]

$HClO_4$,[8] H_2SO_4+$K_2Cr_2O_7$,[9,10] and H_2SO_4+$KMnO_4$,[11] remained as the main class of oxidants that have been reported in the literature, though several other oxidants (e.g. OsO_4, H_2O_2) have also been used.

The oxidation reactions discussed above often generate various functional groups (e.g. -COOH, -OH, -C=O) at the opened end or defect sites of the carbon nanotube structure (Scheme 1). Other groups may be also introduced due to side reactions. For example, a small amount of sulfur-containing groups may be introduced onto the H_2SO_4/HNO_3-oxidized carbon nanotubes, as shown in Scheme 2.[7]

The degree of oxidation depends strongly on the nature of the oxidant and reaction conditions. More interestingly, SWNTs and MWNTs behave differently towards the oxidation reactions. As SWNTs are known to exist in bundles, the oxidation reactions take place at the nanotube end-tips and the outer layer of the bundle.[5] Although the oxidation of MWNTs also starts from the nanotube tips and/or the defect sites, the reaction front gradually moves from the outermost graphitic layer toward the nanotube core, leading to a successive removal of the graphene cylinders and thinner nanotubes.[1,12,13] Due to the relatively high reactivity associated with the opened nanotube tips, the oxidized nanotubes often show a larger internal diameter near the open end than within the tube.[14,15] A wide range of techniques, including spectroscopy (FT-IR, UV/vis/NIR,
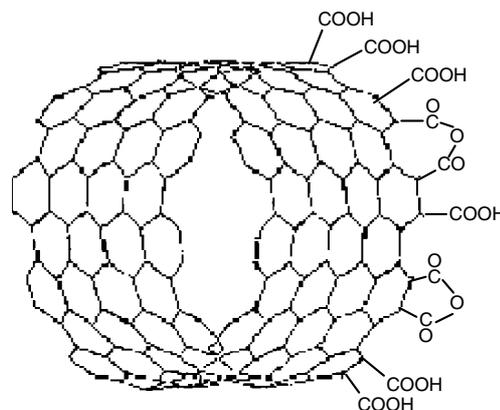
Scheme 1.
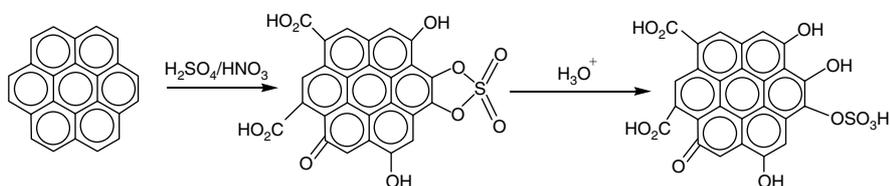
Scheme 2.

Liming Dai received his B.Sc. from Zhejiang University in 1983 and completed his Ph.D. at the Australian National University in 1990. He was a postdoctoral fellow in the Cavendish Laboratory at Cambridge University (1990–1992) and a visiting research faculty member in the University of Illinois at Urbana-Champaign (1992). Thereafter, he had worked in the CSIRO Molecular Science in Melbourne for ten years before he returned to the U. S. in early 2002. He is currently an Associate Professor of Polymer Engineering at the University of Akron, where his group works on the synthesis and micro-/nano-fabrication of functional polymers and carbon nanomaterials. He has received the IBC Award for Achievement in 1995 and IUPAC Young Observer Award in 2003. He also serves as an Editorial Board Member for the Journal of Nanoscience and Nanotechnology *and a Regional Receiving Editor for the* Australian Journal of Chemistry.

Tao Ji received her B.S. in chemistry in 1992 from Nan Kai University, where she then obtained her M.S. degree in polymer chemistry in 1995. Thereafter, she moved on to the Institute of Chemistry, the Chinese Academy of Sciences, to continue her graduate study and received her Ph.D. degree in 1999 on the synthesis and characterization of linear-dendritic copolymers. Following postdoctoral studies at Polytechnic University at Brooklyn, NY, she joined Liming Dai's group at the University of Akron in March 2003 to undertake research on the synthesis of novel light emitting polymers and modification of carbon nanotubes.

Tong Lin obtained his B.Sc. and M.S. from the East China University of Science and Technology, and his Ph.D. from the Chinese Academic of Sciences in 1998, working on functional dyes. He then joined the Molecular Science Centre, Chinese Academic of Sciences, working on hyperbranched conjugated polymers for luminescent applications, before moving to CSIRO Molecular Science, Australia, as a visiting scientist. In 2002 he joined Liming Dai's group in Akron, as a postdoctoral researcher working on carbon nanotubes, and in 2003 returned to Australia for a position at Deakin University.

Vardhan Bajpai was born and brought up in Allahabad, India. He obtained his B.Tech. degree in chemical engineering from Banaras Hindu University in 1998. He then joined the Indian Petrochemical Corporation Ltd. (now Reliance Ltd.) as a production engineer. To further his knowledge, in 2001 he commenced his Ph.D. studies under Liming Dai's supervision.

Raman),[16,17] near-edge X-ray absorption fine structure,[18] electron microscopy (SEM/TEM),[19] EDS, STM,[20] XPS,[7] and X-ray diffractometry,[15] have been used to characterize the oxidized nanotubes.

Covalent Coupling via the Oxidized Nanotube Ends

The carboxylic acid and hydroxyl groups of the oxidized nanotubes can be further used to covalently connect other small and polymeric molecules through reactions characteristic of the -COOH and -OH functionalities. In this context, the reactions of molecular fluorine, rhodamine B, and *p*-carboxytetraphenylporphine (TPP) with the oxidized nanotubes have been reported, Scheme 3.[21]

Similarly, long alkyl chains and/or polymers have been chemically attached onto the oxidized nanotubes through, for example, an amidation reaction, Scheme 4. In this case, the carboxylic acid functionalized nanotubes were firstly converted into alkyl chloride by treatment with $SOCl_2$; aryl amine then reacts with the alkyl chloride to form an amide bond between the nanotube and the aryl group. The attachment of long hydrocarbon chains onto carbon nanotubes improves the nanotube's solubility significantly,[22,23] allowing the modified SWNTs to be purified by conventional chromatographic techniques.[24]

Alkyl chains have also been covalently attached onto the oxidized nanotubes through a simpler reaction between the carboxylic acid and amine groups, Scheme 5, using a carboxylate–ammonium salt, which also improves the solubility of the nanotubes.[23,25]

Polymers with amino terminal groups, such as poly(propionylethylenimine-*co*-ethylenimine) (PPEI-EI), have also been grafted onto oxidized nanotubes through amide formation, Scheme 6. The resulting polymer-grafted SWNTs and MWNTs are highly soluble in most common organic solvents and water.[26–28]

Apart from the amide linkage, the etherification reaction has also been used to covalently attach alkyl groups and polymers onto oxidized carbon nanotubes. For instance, octadecylalcohol[29] and poly(vinyl acetate-*co*-vinyl alcohol) (PVA-VA)[26] have been successfully grafted onto the oxidized SWNTs to improve solubility, Scheme 7.
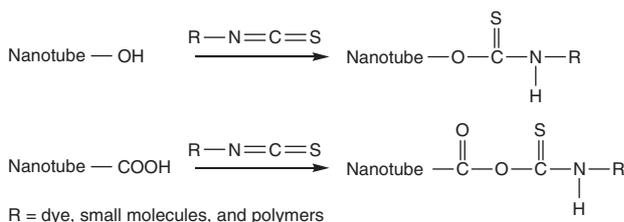
Further, dendrimers or dendrons (e.g. the tenth generation of a poly(amidoamine) (PAMAM) starburst dendrimer)
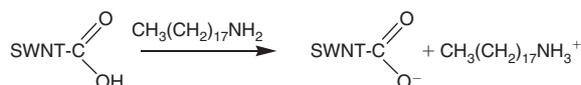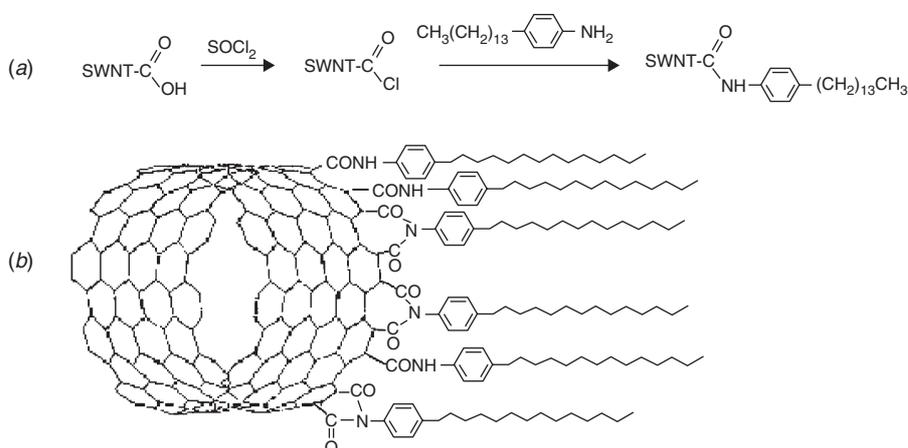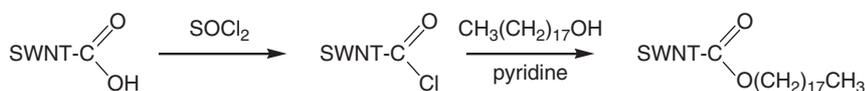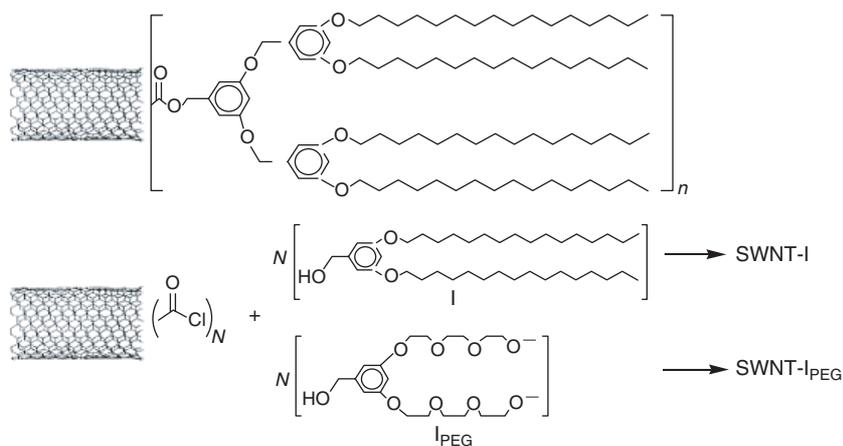
Scheme 5.
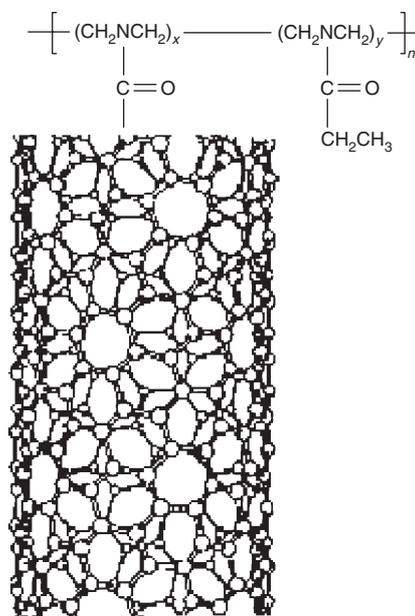
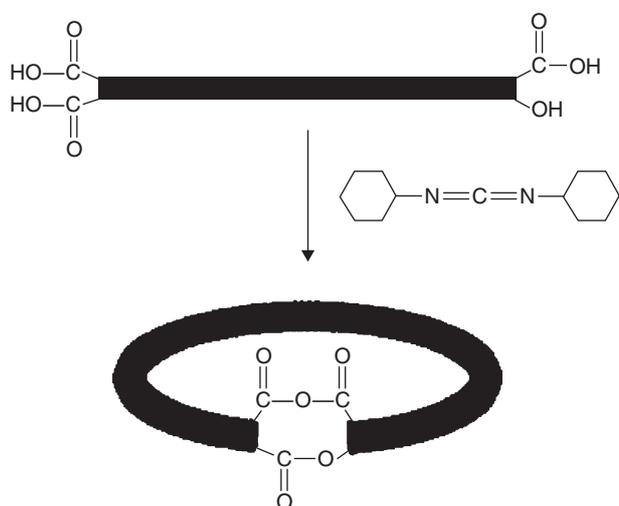**Scheme 6.**

Scheme 3.

Scheme 4.

Scheme 7.

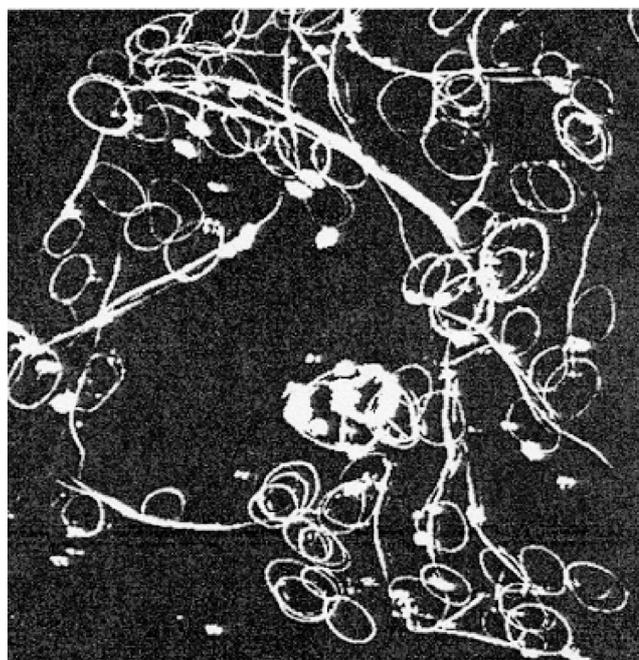**Scheme 8.**

Scheme 9.

Fig. 1. A typical AFM image of carbon nanotube rings. Taken from ref. [33], copyright 2001 AAAS.

have also been grafted onto the oxidized carbon nanotubes to form nanotube stars,[30] Scheme 8, as have lipophilic and hydrophilic dendrons that terminate with long alkyl chains and poly(ethylene glycol) oligomers.[31,32]

Interestingly, Sano et al.[33] reported the ring formation from the acid-oxidized SWNTs through the esterification between the carboxylic acid and hydroxyl end-groups at the nanotube tips in the presence of a condensation reagent, 1,3-dicyclohexylcarbodiimide (Scheme 9). Carbon nanotube rings, with an average diameter of 540 nm and a narrow size distribution, were obtained (Fig. 1).

Nanotube hetero-junctions with two carbon nanotubes joined in either an end-to-side or end-to-end configuration have been constructed through a bi-functionalized amine linkage, as schematically shown in Scheme 10 and Figure 2.[34]

Modification of the Carbon Nanotube Outerwall

Sidewall Fluorination of Carbon Nanotubes

Although carbon nanotubes are generally known to be inert towards fluorine at room temperature, chemical fluorination of carbon nanotubes has been achieved at relatively high temperatures. For instance, Nakajima et al.[35] have demonstrated the chemical fluorination of the carbon nanotube wall at temperatures ranging between 250 and 400°C. Fluorination of SWNTs has also been carried out in the same manner as fluorination of graphite,[36] indicating there was considerable

room for chemical functionalization of carbon nanotubes under appropriate conditions.

Fluorination at a temperature above 400°C was found to cause the decomposition of the nanotube structure. Although
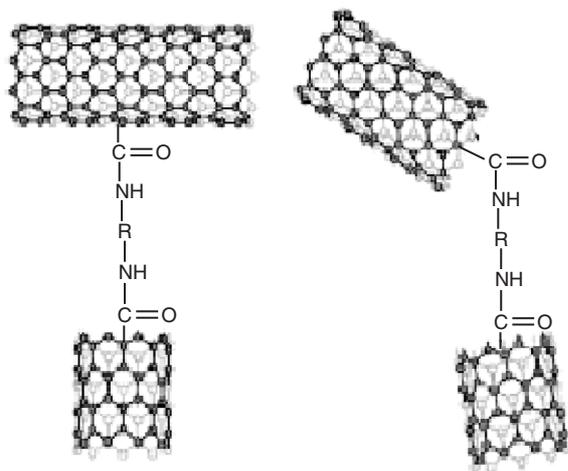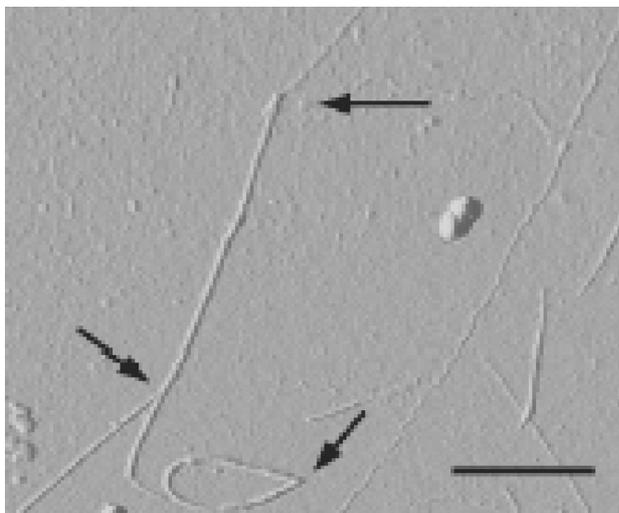

Scheme 10.

Fig. 2. SEM image of the interconnected SWNTs. Taken from ref. [34], copyright 2002 AIP.

fluorination between 250 and 400°C does not damage the structure to that extent, it reduces the conductivity of the SWNTs due to the partial destruction of the graphitic structure. As a result, the electronic properties of the fluorinated SWNTs differ dramatically from those of their unmodified counterparts. The presence of covalently bonded fluorine in the fluorinated carbon nanotube sample was confirmed by the appearance of FT-IR peaks at 1220–1250 cm^{-1}. The TEM elemental images given in Figure 3 further indicate that fluorine atoms are homogeneously attached onto the nanotube wall.

The covalently bonded fluorine was found to be removable from the fluorinated nanotube surface by treatment with hydrazine, Equation (*1*).

$$CF_n + \frac{n}{4}N_2H_4 \rightarrow C + nHF + \frac{n}{4}N_2 \qquad (1)$$
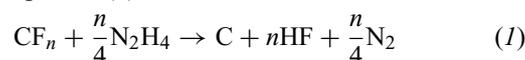
This fluorination reaction is of considerable interest because further functionalization of carbon nanotubes can be carried out through the fluorine intermediate. In this context, it was demonstrated that the covalently bonded fluorine could be replaced by alkyl groups through the alkylation reaction.[37] For this purpose, an alkyllithium or Grignard reagent can be used as an alkylation reagent. Interestingly enough, these alkyl groups can also be removed by heating the alkylated nanotubes at about 250°C, leading to the recovery of the pure SWNTs. Various physicochemical properties of the fluorinated SWNTs, including high-resolution electron energy loss,[38] thermal recovery behaviour,[39] and solvation in alcoholic solvents,[40] have been investigated. Furthermore, Yudanov and coworkers[41] have recently demonstrated the fluorination of MWNTs at room temperature by using BrF$_3$ as the fluorination reagent, although only the outside shell of the MWNT was modified.

The Attachment of Dichlorocarbene to the Sidewall of Carbon Nanotubes

As is well known, 1,1-dichlorocarbene can attack C=C bonds connecting two adjacent six-membered carbon rings to produce 1,1-dichlorocyclopropane, Scheme 11. This reaction has been investigated for both SWNTs and MWNTs[22] using 1,1-dichlorocarbene generated from different sources, including NaOH/CHCl$_3$ and a mercury complex.
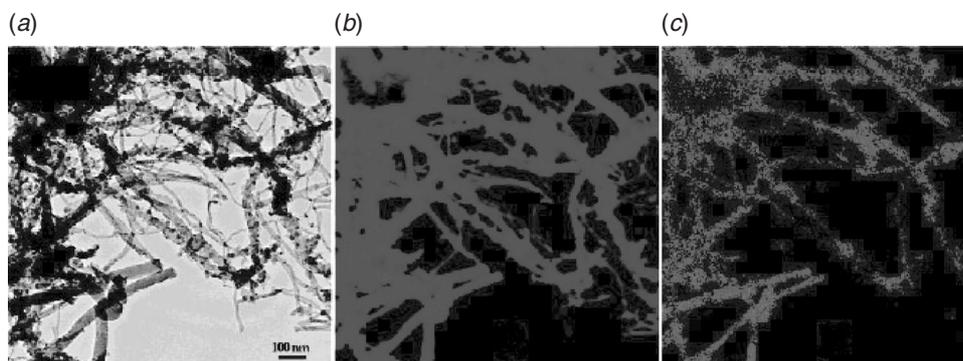

Fig. 3. (*a*) TEM image of fluorinated carbon nanotubes and the corresponding elemental maps for (*b*) carbon and (*c*) fluorine. Taken from ref. [39], copyright 2002 ACS.

The chemical state of carbon and oxygen in carbenated nanotubes has been studied using XPS measurements.[42] A large amount of amorphous carbon was found attached onto the tubular wall, leading to questions on whether the dichloro-carbene attaches onto the sidewall of the nanotube or just reacts with the amorphous carbon.[43]

### Modification via 1,3-Dipolar Cycloaddition of Azomethine Ylides

Like fullerene C_{60}, 1,3-dipolar cycloaddition of azomethine ylides can also take place between the graphite sidewall of SWNTs at the C=C bond connecting two adjacent six-membered rings and a molecule of an α-amino acid or an aldehyde, Scheme 12.[44] Carbon nanotubes thus modified showed a high solubility in chloroform (up to $50\,mg\,mL^{-1}$). Compared with pure SWNT bundles, the modified SWNTs also exhibited somewhat poorer electronic properties with a more densely packed bundle structure, as indicated by TEM and other electronic spectroscopic measurements.

The Reaction between Aniline and Carbon Nanotubes

Recently, it has been found that carbon nanotubes showed strong interactions with aniline.[45] The strong intermolecular interaction facilitates the dissolution of SWNTs in aniline, up to a relatively high solubility of $8\,mg\,mL^{-1}$. Moreover, new UV/vis absorption ($\sim$540 nm) and fluorescence emission ($\sim$620 nm) peaks were observed (Fig. 4). It was a surprise to discover that the interaction between aniline and carbon nanotubes generates these new peaks, as aniline normally quenches fluorescence emission due to its strong electron affinity.[45] However, a chemical reaction might have taken place between the SWNT and aniline, as shown in Scheme 13.
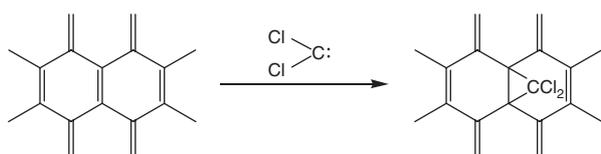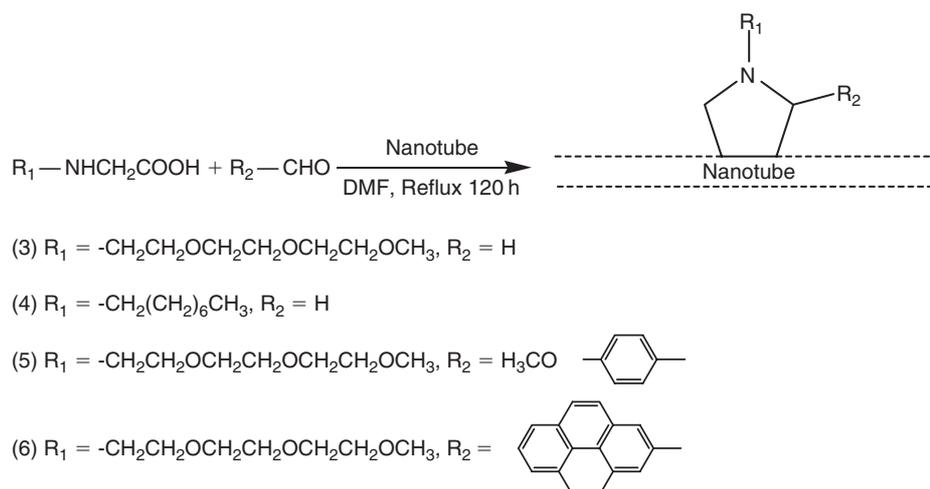
Having demonstrated the modification of a glassy carbon electrode by electrochemical reduction of an aryl diazonium salt, Tour and coworkers[46] were able to demonstrate that this process was also possible with the nanotube electrode. This reaction involves the attachment of aryl cations onto the sidewalls of SWNTs. A variety of diazonium salts have been attached to the nanotube wall (Scheme 14). The nature of the C4 substitution of the benzyl group plays an important role in regulating the degree of grafting and the solubility of the resulting product. Those aryl cations with long alkyl
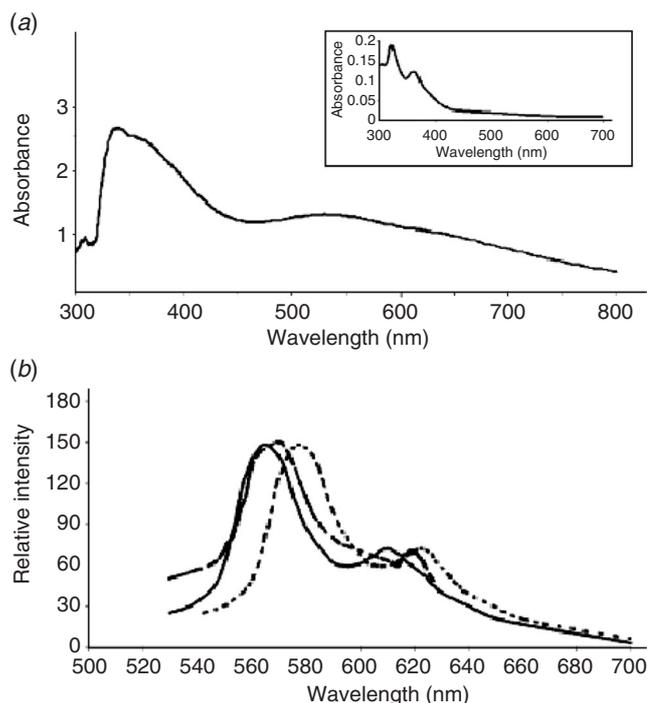
Fig. 4. (*a*) UV/vis absorption spectrum of a carbon nanotube dissolved in aniline. Inset: The corresponding spectrum for the carbon nanotube–aniline solution diluted with acetone. (*b*) Fluorescence emission spectra of the carbon nanotube–aniline solution diluted in different solvents: acetone (- - -), toluene (-·-·), and methanol (—); all samples were excited at 500 nm. Taken from ref. [45], copyright 2001 ACS.

Scheme 11.

(3) R_1 = -CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$, R_2 = H

(4) R_1 = -CH$_2$(CH$_2$)$_6$CH$_3$, R_2 = H

(5) R_1 = -CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$, R_2 = H$_3$CO

(6) R_1 = -CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$, R_2 =

Scheme 12.

Scheme 13.

Br— (1) N₂⁺BF₄⁻

Cl— (2) N₂⁺BF₄⁻

F— (3) N₂⁺BF₄⁻

(4) N₂⁺BF₄⁻

O₂N— (5) N₂⁺BF₄⁻

H₃CO₂C— (6) N₂⁺BF₄⁻

(7) N₂⁺BF₄⁻

(8) NO₂ N₂⁺BF₄⁻

(9) N₂⁺BF₄⁻

Scheme 14.

Scheme 15.

of a nanoporous template (e.g. an alumina membrane or a mesoporous zeolite). The template synthesis often allows the production of monodispersed carbon nanotubes with opened ends as well as controllable diameters, lengths, and orientations. Therefore, the nanoporous alumina membrane-assisted deposition of aligned carbon nanotubes[48,49] and the preparation of carbon nanotubes by high-temperature graphitizing of polyacrylonitrile (PAN) nanotubules synthesized within the pores of an alumina template membrane or zeolite nanochannels are of particular interest.[50,51] Based on the template method for the nanotube growth, Kyotani et al.[47] have successfully carried out the nitric acid oxidation of nanotube innerwalls within the pores of nanoporous alumina, in which the template acts as a protective layer for the outerwall. Upon the completion of the innerwall oxidation, the template was removed by dissolving it in aqueous HF, thereby releasing the innerwall-modified nanotubes (Scheme 15).

Other Physical Chemistries of Carbon Nanotubes

Modification of Carbon Nanotubes via Mechanochemical Reactions

Mechanochemistry refers to processes in which mechanical motions control chemical reactions.[52] Specifically, the mechanochemical reaction involves highly reactive centres generated by mechanical energy (e.g. ultrasonication or ball-milling) imparted to the reaction system. Certain organic reactions have been demonstrated to take place efficiently in the solid state.[53]

Ultrasonication has been demonstrated to significantly enhance many chemical reactions, including the acid oxidation of carbon nanotubes.[54] It was envisaged that the strong vibration arising from the ultrasonication created many defect sites on the SWNT sidewalls (both the inner and outer ones), which could not only facilitate the oxidation reaction but also cleaved the SWNTs into short segments. Ultrasonication has also been found to induce a chemical reaction between SWNTs and monochlorobenzene in the presence of poly(methyl methacrylate) (PMMA).[55] In
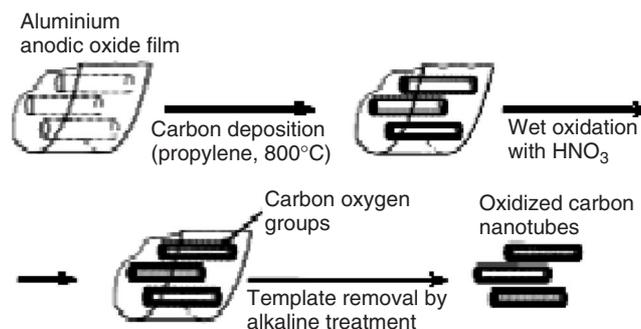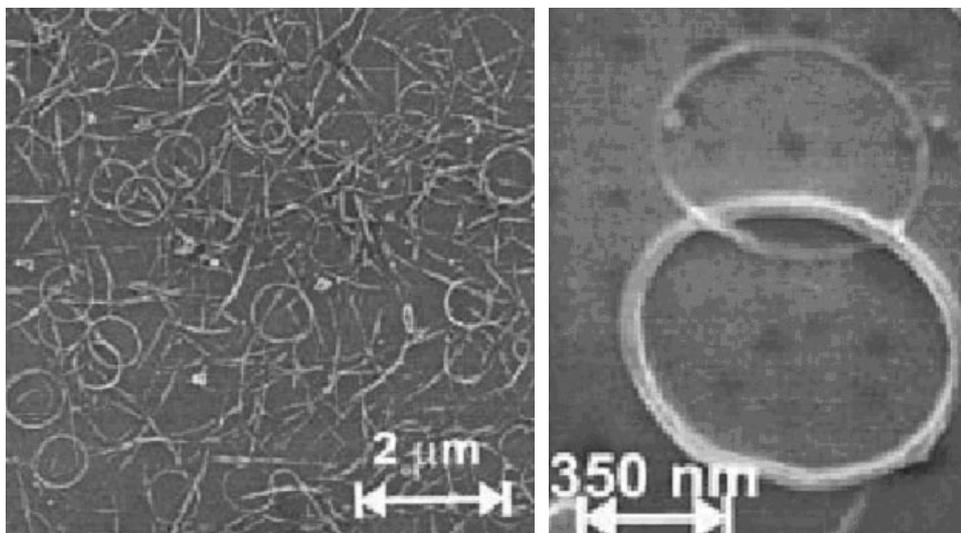
chains at the *para*-position of the benzyl ring can significantly improve the solubility of carbon nanotubes in organic solvents. The grafted moieties can be removed by simply heating the modified carbon nanotubes in an inert atmosphere at 500°C.

Functionalization of the Carbon Nanotube Innerwall

Compared with the outerwall modifications discussed above, the functionalization of the nanotube innerwall is much less discussed in the literature. This is because innerwall modifications often require opening the nanotube tip(s) and protection of the outerwall; these processes are complicated and tedious. In this regard, carbon nanotubes synthesized by the template technique possess advantages towards innerwall modification.[47]

The template technique involves direct deposition of carbon nanotubes, or their precursor polymer nanotubes followed by high-temperature graphitizing, within the pores

Fig. 5. Nanotube rings formed by ultrasonication. Taken from ref. [58], copyright 1999 ACS.
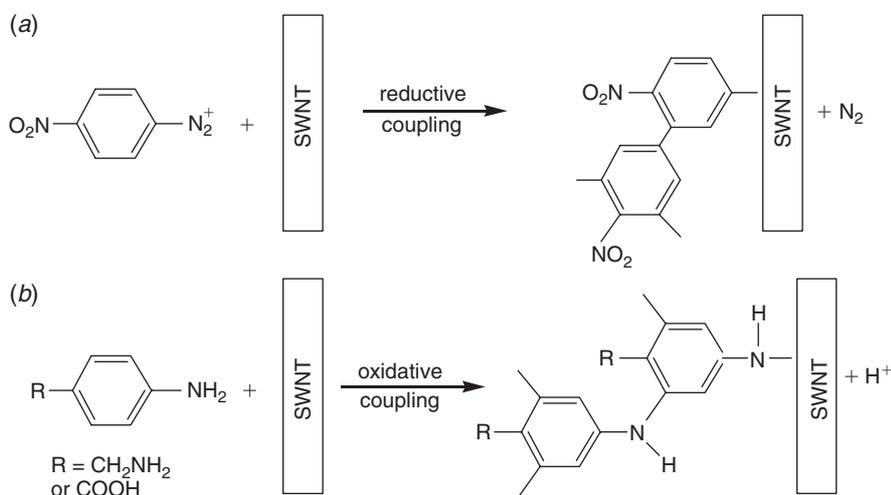
Scheme 16.

particular, SWNTs could be separated from carbonaceous impurities and degraded to short segments by ultrasonicating SWNTs and PMMA in chlorobenzene.[55] As indicated by the appearance of new peaks at 1729, 2848, and 2920 cm^{-1}, characteristic of C=C, C=O, and C–H stretching vibrations, respectively, in solid-state diffuse reflectance FT-IR spectra, the above polymer-assisted ultrasonication purification process was accompanied by a chemical reaction between the SWNT and chlorobenzene.[56] PMMA might have enhanced the solubility of SWNTs in chlorobenzene, and hence facilitated the reaction. High-resolution TEM imaging revealed that a large number of defects formed in the sidewall of SWNTs, which became holes upon heating in oxygen.[57]

Another closely related observation is that certain SWNTs folded under ultrasonication to form nanotube coils with a narrow distribution (300–400 nm) of radii, as shown in Figure 5.[58] Although the ultrasonication-induced nanotube ring formation seemed, unlike those nanotube rings formed by the end-to-end ester linkage discussed above (Scheme 9),[33] to be largely a physical process, some

interesting chemical interactions between the nanotube ends might be involved as very smooth junctions were observed.

Apart from ultrasonication, various other physicochemical processes, including microwave irradiation[59] and ball-milling,[60] have also been investigated. In particular, ball-milling of carbon nanotubes in the presence of acid was reported to cleave the nanotubes into 200–300 nm long ropes.[60]

Modification of Carbon Nanotubes via Electrochemical Reactions

Owing to the good electronic properties intrinsically associated with carbon nanotubes,[61] electrochemical modification of individual carbon nanotube bundles has been attempted. To demonstrate this, Kooi et al.[62] electrochemically polymerized a thin polymer layer onto the individual SWNT bundle (Scheme 16), which was pre-coated on a microelectrode. The resultant polymer layer was directly observed to be of 6 nm thickness, by means of in situ AFM imaging (Fig. 6).
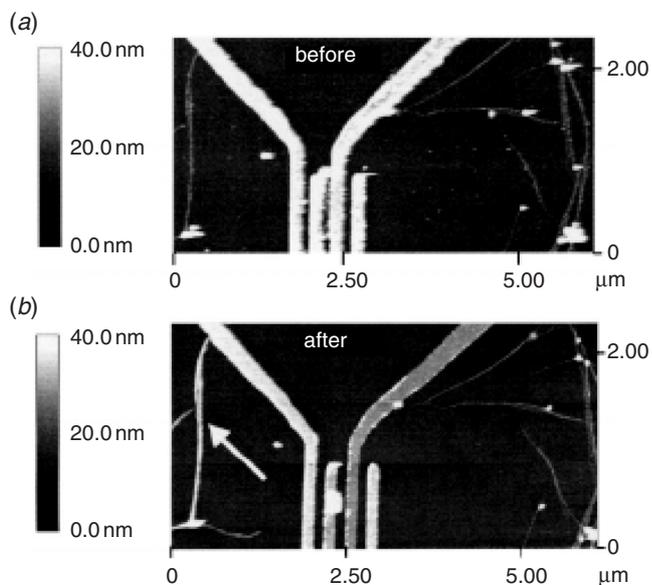
Fig. 6. AFM image of SWNTs (*a*) before and (*b*) after reductive coupling with a polymer. Taken from ref. [62], copyright 2002 Wiley-VCH.

Modification of Carbon Nanotubes via Photochemical Reactions

Despite of the well-known fact that carbon nanotubes possess unusual optoelectronic properties, the recent report on ignition of some dry and fluffy SWNTs in air by the camera flash is rather intriguing.[63] In view of the highly efficient absorption of light by carbon nanotubes, the observed ignition may be resulted from a rapid temperature increase within the nanotube sample upon exposure to the flash (estimated to heat to 1500°C in a very short time), which is well above the temperature required for ignition when oxygen is present. While the mechanism of ignition by a camera flash in this system deserves further investigation, such an interesting photochemical reaction may find its application in the remote light-triggered combustion or explosives.[63]

Closely related to the above discussion, band gap fluorescence emission from individual SWNTs has also been observed. For instance, O'Connell et al.[64] obtained individual nanotubes through ultrasonication of an aqueous dispersion of raw SWNTs in sodium dodecyl sulfate, followed by centrifuging to remove tube bundles, ropes, and residual catalyst. They found that individual semiconducting carbon nanotubes could show fluorescence emission directly across the band gap, whereas aggregation of the nanotubes into bundles quenches the fluorescence through interactions with metallic tubes, thereby substantially broadening the absorption bands. More recently, incandescent light emission has also been observed from certain carbon nanotubes upon the application of a DC voltage.[65] Continued research efforts in this embryonic field could lead to nanotube optoelectronic technologies.

Non-Covalent Chemistry of Carbon Nanotubes

Non-covalent chemistry involves self-assembly of molecules or macromolecules to thermodynamically stable structures that are held together by weak, non-covalent interactions. These weak non-covalent interactions include hydrogen bonding, π–π stacking, electrostatic forces, van der Waals forces, and hydrophobic and hydrophilic interactions. Because of the rapid dynamics and very specific non-covalent interactions involved, self-assembling processes are usually very fast. The resulting supramolecules could undergo spontaneous and continuous de- and re-assembly processes under certain conditions due to the non-covalent nature. Non-covalent supramolecules can, therefore, select their constituents in response to external stimuli or environmental factors and behave as adaptive materials. Although self-assembling (or non-covalent chemistry) of small molecules and certain macromolecules has been an active research area for some time, the non-covalent chemistry of carbon nanotubes is a recent development. Non-covalent chemistry, however, offers an important advantage in not changing the carbon nanotube's structure, and hence its electronic properties are largely retained. A literature survey shows that a few of non-covalent methods, including the self-assembling of planar π-systems[66] and wrapping polymer chains onto the nanotube surface[67] have been successfully devised for modification of carbon nanotubes, as described below.

Non-Covalent Attachment of Small Molecules onto the Sidewall of Carbon Nanotubes

Chen et al.[66] have recently found that certain aromatic molecules with a planar π-moiety (e.g. pyrenylene) could strongly interact with the basal plane of graphite on the nanotube sidewall via π-stacking. The interaction is so strong that the aromatic molecule is irreversibly adsorbed onto the hydrophobic surface of carbon nanotubes, leading to a highly stable, self-assembled structure in aqueous solutions. As schematically shown in Scheme 17, the long alkyl chains, end-adsorbed onto the nanotube surface via the aromatic anchors, could significantly improve the solubility of the nanotubes.

The above approach could be used to attach biochemically active molecules, such as DNA and proteins, on the sidewall of SWNTs through appropriate anchoring molecules. For example, some amine-containing bioactive molecules, including ferritin, streptavidin, and biotinyl-3,6-dioxactanediamine, have been attached onto the sidewall of SWNTs through a nucleophilic substitution of the amino functionality by an *N*-hydroxysuccinimide group, which was pre-anchored onto the nanotube surface through a succinimidyl ester linkage by pyrenylene (Scheme 18 and Fig. 7).[66]

Non-Covalent Wrapping of Polymer Chains onto the Sidewall of Carbon Nanotubes

Like the π-conjugated small molecules, many high molecular weight polymers (especially conjugated polymers) showed the ability to wrap around the surface of carbon nanotubes.[67–76] The wrapping of polymer chains around SWNTs could reduce the intertube van der Waals interaction, and hence enhance the solubility of SWNTs. Strong π–π interactions between carbon nanotubes and conjugated
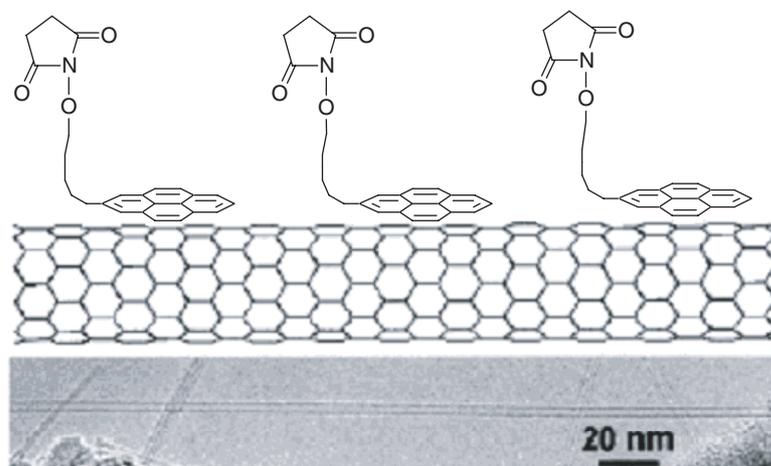
Scheme 17.
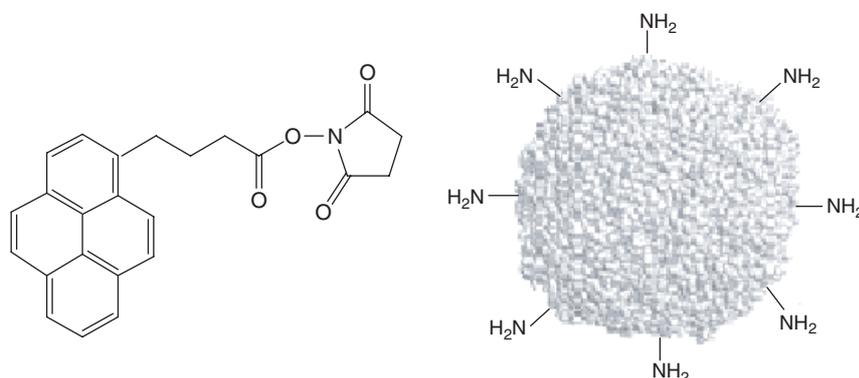
Scheme 18.
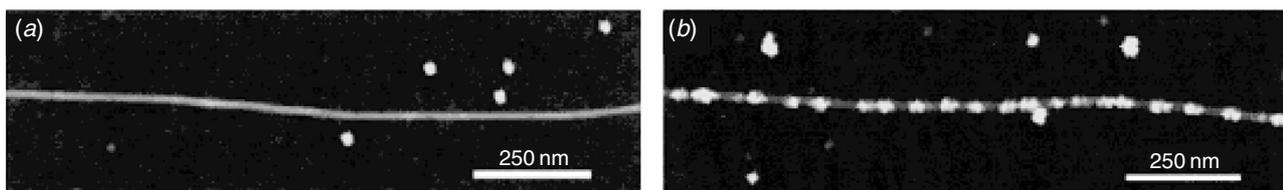
Fig. 7. AFM images showing (*a*) a SWNT bundle (diameter 4.5 nm) free of absorbed ferritin after incubation in a ferritin solution and (*b*) ferritin molecules (apparent heights ∼10 nm) adsorbed on a SWNT bundle (diameter 2.5 nm) functionalized by succinimidyl ester (Scheme 18) and included in a ferritin solution. Taken from ref. [66], copyright 2001 ACS.

polymers has led to the wrapping of such as poly(*m*-phenylenevinylene) (PmPV) chains around the carbon nanotube sidewall, as schematically shown in Figure 8.

The wrapping process is, at least partially, indicated by the broadening effect on the UV/vis absorption bands at 329 and 410 nm, characteristic of PmPV, and the appearance of a new broad absorption band over 650–900 nm, from the SWNTs/PmPV complexes, as shown in Figure 9.[77]

Similarly, conjugated-polymer wrapped carbon nanotubes have also been prepared by in situ polymerization of phenylacetylene (PA) in the presence of shortened SWNTs.[78] Characterization of the resulting material by GPC, NMR, UV/vis, SEM/TEM, and XRD revealed that the PPA chains thickly wrapped the nanotubes. The SWNT/PPA composites exhibit a high solubility in organic solvents, good photostability even

under harsh laser irradiation, and excellent optical limiting properties.

Self-Assembly of Modified Carbon Nanotubes

Apart from the aligned/micropatterned growth of carbon nanotubes,[79,80] ordered structures have been so far only constructed from a few of the end-functionalized carbon nanotubes on certain pre-treated substrates. For instance, Liu et al.[81] have prepared aligned SWNTs by self-assembling nanotubes, which have been end-functionalized with thiol groups, onto a gold substrate (Scheme 19). The carboxylterminated short SWNTs prepared by acid oxidation were used as the starting material for further functionalization with thiol-containing alkyl amines through the amide linkage. The
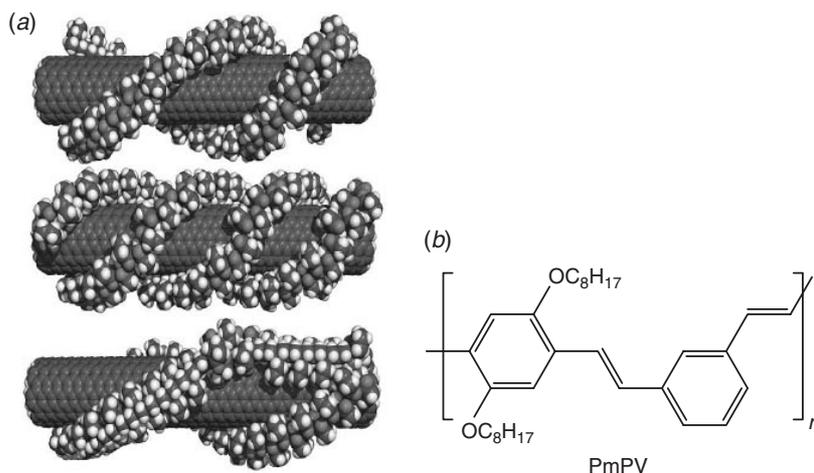
Fig. 8. (*a*) Some possible wrapping arrangements of PmPV on a SWNT. A double helix (top) and a triple helix (middle). Backbone bond rotations can induce switch-backs, allowing multiple parallel wrapping strands to come from the same polymer chain (bottom). (*b*) Structure of PmPV. Taken from ref. [69], copyright 2001 Elsevier.
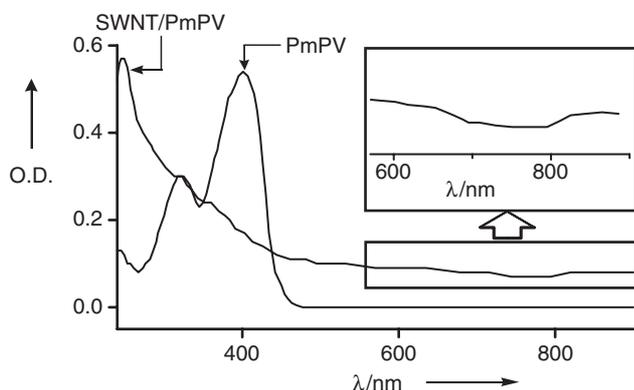
Fig. 9. UV/vis spectra of PmPV and the SWNT–PmPV complex. Taken from ref. [77], copyright 2002 ACS.

self-assembly of aligned SWNTs was obtained by dipping a gold(111) ball into the thiol-functionalized SWNT suspension in ethanol, followed by ultrasonication and drying in high-purity nitrogen.

The resulting self-assembled aligned nanotube film is so stable that ultrasonication cannot remove it from the gold substrate. The packing density of the self-assembled aligned carbon nanotubes was found to strongly depend on the incubation time. As seen in the AFM images of Figure 10, an assembly of shorter nanotubes with a lower packing density was formed with a brief adsorption time, whereas longer adsorption times resulted in the formation of aligned nanotube array of longer mean length and higher packing density.

Given that carboxylic acids could be deprotonated by various metal oxides (e.g. silver, aluminium, or copper oxide), Liu and coworkers[82] have investigated the formation of aligned nanotube arrays by self-assembling COOH-terminated carbon nanotubes onto certain metal oxide substrates. The deprotonation between the carboxylic groups on nanotubes and the metal surface effectively led to the anchoring of aligned carbon nanotubes on the metal substrate via their carboxylated

anionic head groups by Coulombic forces. Although Raman spectroscopic measurements seemed to confirm the process illustrated in Scheme 20,[82] it deserves further investigation with various other techniques.
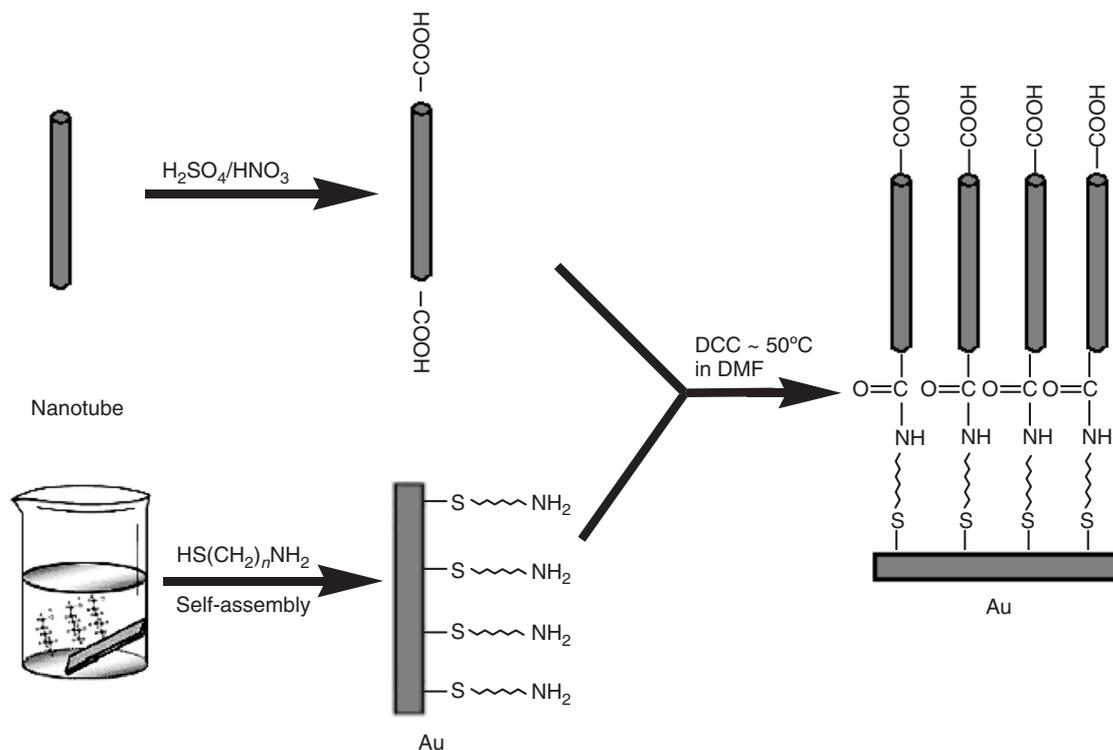
Recently, Nan et al.[83] have demonstrated that individual acid oxidized SWNTs can be deposited onto a gold substrate pre-treated with $NH_2(CH_2)_{11}SH$ to form an aligned nanotube array on gold through the amide linkage (see Scheme 19). In this case, the microcontact printing (μCP) technique was used to pre-pattern the thiol self-assembled monolayer on the gold surface for region-specific deposition of the aligned carbon nanotubes. As shown in the optical microscope image (Fig. 11*a*), the dark dot regions are covered by carbon nanotubes. The corresponding AFM image given in Figure 11*b* clearly shows the aligned structure.

More recently, Guo and coworkers[84] have developed a new approach to modify carbon nanotubes with multiple hydroxyl groups ('carbon nanotubols') via a simple solid-phase mechanochemical reaction with potassium hydroxide at room temperature. The carbon nanotubols thus produced are highly soluble in water and can readily self-assemble into aligned arrays upon drying.

As shown in Figure 12*a*, the SEM image for the starting SWNTs shows a randomly entangled morphology. In contrast, the cross-section SEM image of a centrifuged nanotubol film, prepared by ball-milling buckypaper in the presence of KOH,[84] reveals self-assembled arrays with a well-aligned structure (Fig. 12*b*). Figure 12*c* indicates the occurrence of a large-scale self-assembling process. As schematically illustrated in Figure 12*d*, the strong hydrogen bonding interaction between the nanotubols is believed to be the driving force for the formation of the highly oriented, self-assembled arrays.

Modification of Aligned Carbon Nanotubes

The use of carbon nanotubes, either in their aligned or non-aligned form, for many applications, including as a

Scheme 19.

H$_2$SO$_4$/HNO$_3$

Nanotube

COOH — COOH

HS(CH$_2$)$_n$NH$_2$
Self-assembly

S ⁓⁓ NH$_2$
S ⁓⁓ NH$_2$
S ⁓⁓ NH$_2$
S ⁓⁓ NH$_2$

Au

DCC ~ 50°C
in DMF

COOH COOH COOH COOH

O=C O=C O=C O=C

NH NH NH NH

S S S S

Au

(a) 100 nm (b) 100 nm (c) 50 nm
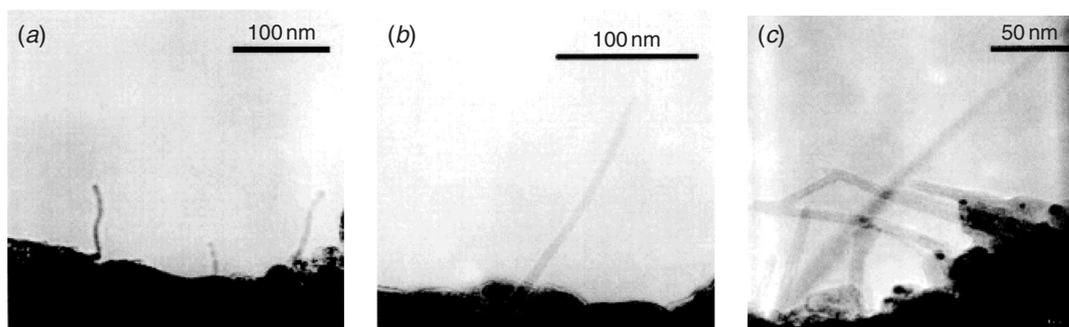
Fig. 10. (a) A shorter nanotube assembly with a lower packing density was formed with a shorter adsorption time but (b, c) longer adsorption times result in the formation of an aligned nanotube array with a longer mean length and a higher packing density. Taken from ref. [82], copyright 2001 ACS.

H$_2$SO$_4$/HNO$_3$
Cutting

COOH — COOH

Self-assembly

COOH COOH COOH COOH

C C C C
O O O O O O O O

Ag$^+$ Ag$^+$ Ag$^+$ Ag$^+$
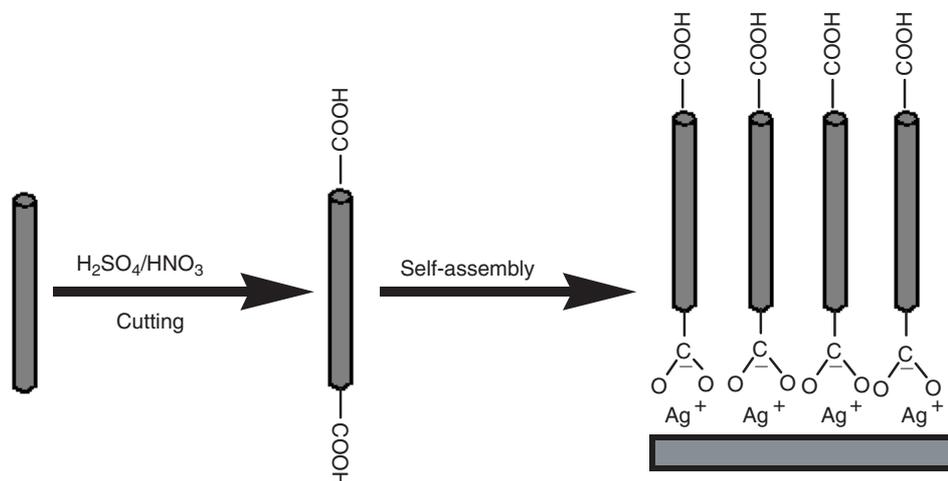
Scheme 20.
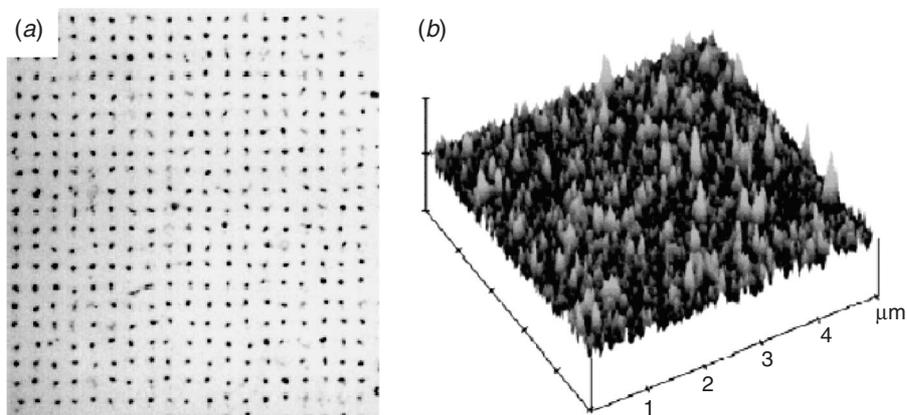
Fig. 11. Aligned carbon nanotubes formed by self-assembling COOH-terminated nanotubes on a gold surface pre-patterned with thiol molecules. (*a*) Optical microscope and (*b*) AFM images. Taken from ref. [83], copyright 2002 Elsevier.
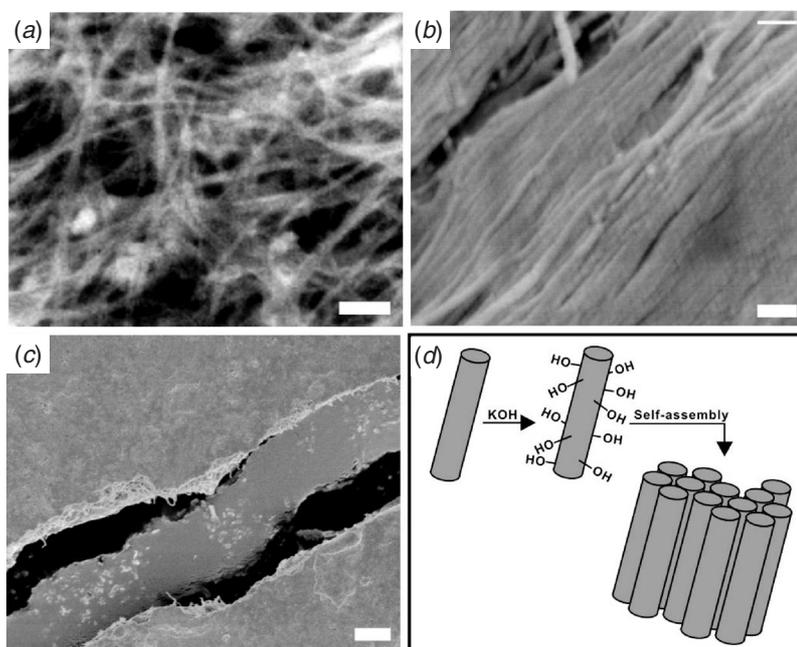
Fig. 12. SEM images of (*a*) the starting materials (Tube@Rice; scale bar 100 nm), (*b*) the aligned tubes at a higher magnification view (scale bar 100 nm), and (*c*) a top view of the aligned carbon nanotubols (scale bar 1 μm). (*d*) A cartoon of the self-assembly process. Taken from ref. [84], copyright 2003 ACS.

reinforcement agent in advanced polymer composites and as biosensors or artificial muscles in biomedical devices, inevitably require modification of their surface characteristics to meet the specific requirements for particular applications. Due to the rather harsh conditions involved, however, most of the above-mentioned solution reactions would damage the aligned carbon nanotubes detrimentally. Given that the alignment is an additional advantage for the use of carbon nanotubes in many devices, a particularly attractive option is the surface modification of carbon nanotubes whilst largely retaining their structural integrity.

Plasma Activation of Aligned Carbon Nanotubes

Dai and coworkers[85–87] have developed a novel approach for chemical modification of aligned carbon nanotubes by carrying out radio-frequency glow-discharge plasma treatment, and subsequent reactions characteristic of the plasma-induced surface groups. For instance, they have successfully immobilized polysaccharide chains onto acetaldehyde–plasma activated carbon nanotubes through the Schiff-base formation, followed by reductive stabilization of the Schiff-base linkage with sodium cyanoborohydride in water under mild conditions (Scheme 21). The resulting amino-dextran grafted nanotube film showed a high hydrophilicity.[87] These authors have also used the plasma technique for purifying and controlled opening of the aligned MWNTs. As seen in Figure 13, water plasma etching removed the catalyst tip of aligned carbon nanotubes without damaging the aligned structure.[86] Therefore, plasma etching could facilitate the surface modification of the nanotube innerwall.
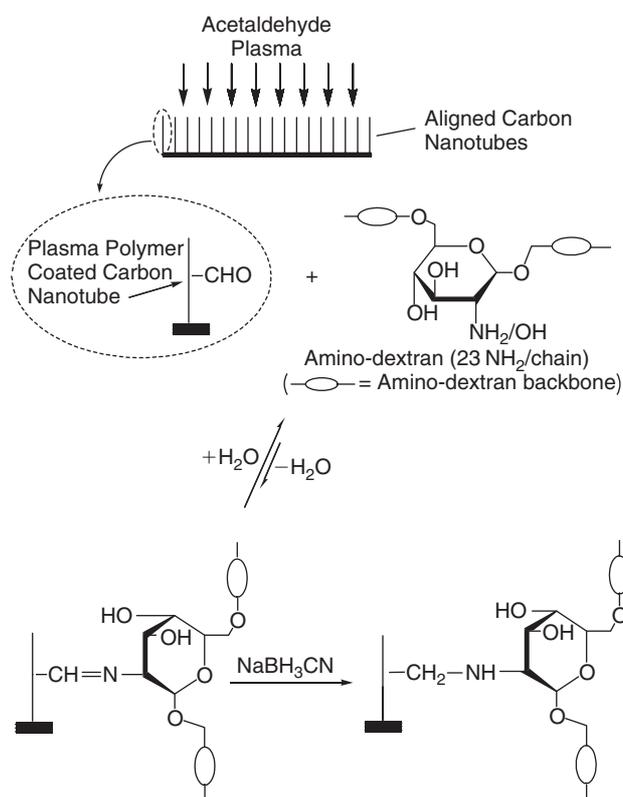
Scheme 21.
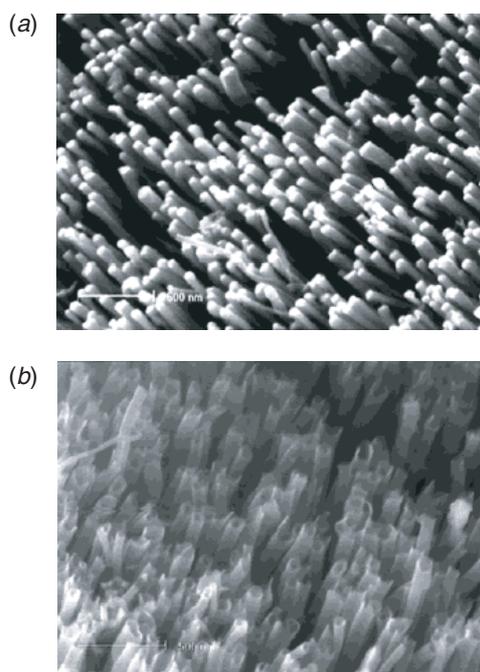
Fig. 13. Aligned carbon nanotubes (*a*) before and (*b*) after their tips were removed by a water plasma treatment. Taken from ref. [86], copyright 2002 ACS.

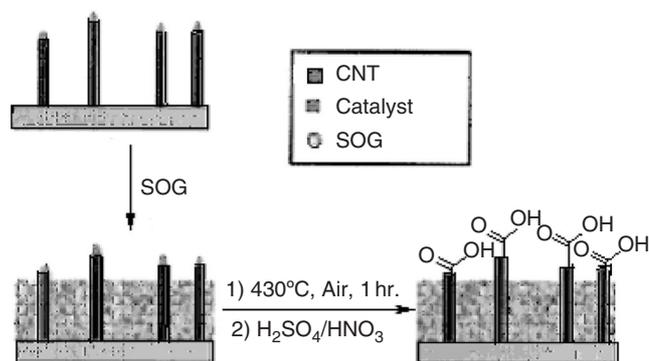Similarly, Khare et al.[88] have recently reported the cold hydrogen-plasma treatment for SWNTs. In situ FT-IR measurements revealed CH_2 and CH_3 bands at 2924, 2955, 2871, 2863, and 2854 cm^{-1} as well as the bending mode of C–H vibrations at 1370 and 1459 cm^{-1} after the plasma irradiation

Fig. 14. Cartoon of the fabrication and pretreatment of the aligned carbon nanotubes for further functionalization. Taken from ref. [89], copyright 2002 ACS.

of hydrogen. The plasma modification was further confirmed by the deuterium replacement study, with C–D stretching bands being seen at 2000 and 2250 cm^{-1}.

Acid Oxidation with Structural Protection

In view of the fact that oxidative treatment of aligned carbon nanotubes in solution for generating carboxylic and/or hydroxyl groups for further chemical modification often leads to the total collapse of the aligned nanotubes, Meyyappan and coworkers[89] developed an interesting method to protect the alignment structure by filling the gaps between the aligned nanotubes with a spin-on glass (SOG) prior to the oxidative reaction (Fig. 14). Figure 15 shows the oxidation-induced changes in alignment for the aligned carbon nanotubes with and without the SOG protection. Comparison of Figures 15*C* and 15*B* indicates that the SOG film provides structural support to the aligned carbon nanotubes.

After having successfully functionalized the tips of the aligned carbon nanotubes with carboxylic groups, these authors demonstrated accomplishments in chemical coupling of nucleic acids to the aligned nanotube array using the standard water-soluble coupling reagents, such as EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride) and sulfo-NHS (*N*-hydroxysulfo-succinimide), as schematically shown in Scheme 22.

Electrochemical Modification of Aligned Carbon Nanotubes

Another interesting area closely related to the above chemical modification of aligned nanotube surfaces is the synthesis of coaxial nanowires of polymers and carbon nanotubes. In this regard, Dai and coworkers[90] have recently used aligned carbon nanotubes as nanoelectrodes for making coaxial nanowires by electrochemically depositing a concentric layer of a conducting polymer uniformly onto each of the aligned nanotubes, to thereby form aligned, conducting-polymer-coated carbon nanotube (CP-NT) coaxial nanowires. The SEM image for these CP-NT coaxial nanowires, given in Figure 16*b*, shows the same features as the aligned nanotube array of Figure 16*a*, but the former has a larger tubular diameter due to the presence of the newly electropolymerized polypyrrole coating.
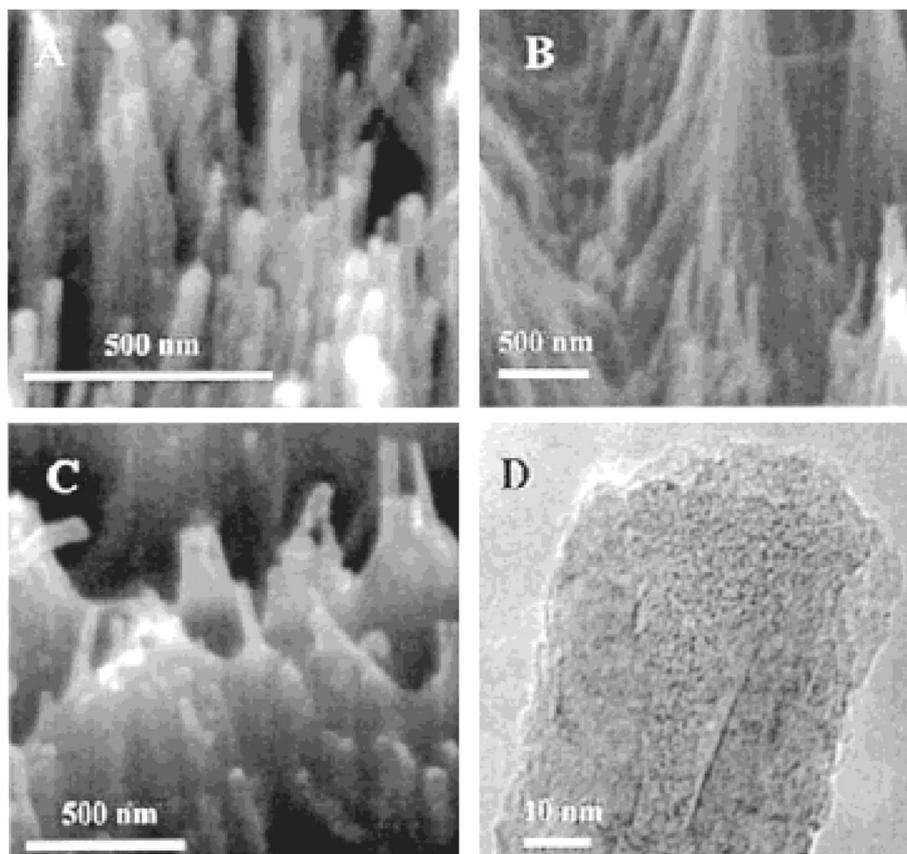
Fig. 15.   SEM images of (*A*) vertically aligned carbon nanotube arrays, (*B*) the collapsed carbon nanotube array without SOG after the oxidative treatment, and (*C*) the aligned carbon nanotube array with SOG after the oxidative treatment. (*D*) High resolution TEM image of the opened carbon nanotube. Taken from ref. [89], copyright 2002 ACS.

$$1 = H_2N(CH_2)_6-R_1-Cy3$$
$$R_1 = AAAAACCCTTTTTTGGAAAAA$$
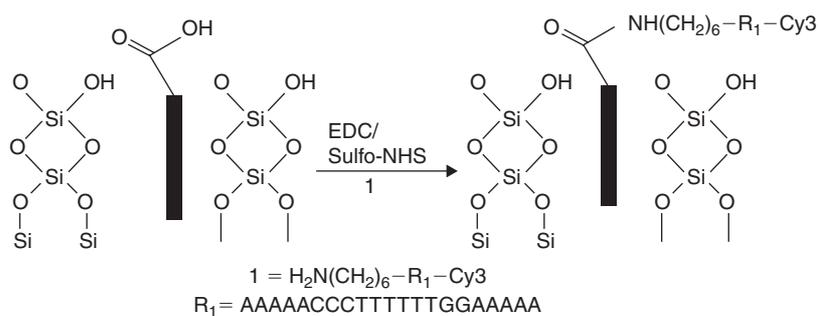
Scheme 22.
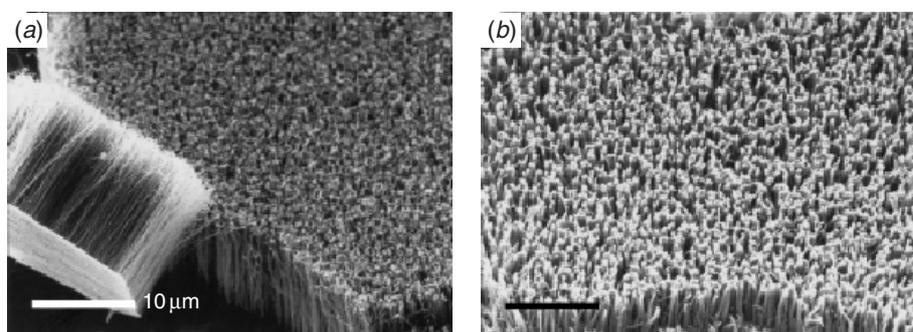
Fig. 16.   (*a*) Aligned nanotubes and (*b*) CP-NT coaxial nanowires. Taken from ref. [90], copyright 2000 Wiley-VCH.

The presence of the conducting polymer layer was also clearly evident in TEM images and by the much stronger redox responses of the conducting polymer layer when coated on the nanotube surface than that of the same polymer on a conventional flat electrode under the same conditions.[90] The coaxial structure allows the nanotube framework to provide mechanical stability and efficient thermal and electrical contact with the conducting polymer layer. The large interfacial surface area per unit mass obtained for the nanotube-supported conducting polymer layer is potentially useful in many optoelectronic applications, for example in sensors, organic light-emitting diodes, and photovoltaic cells, where the charge injection and separation are strongly limited by the interfacial area available in more conventional devices.

Conclusions

Depending on their diameter and helicity of the arrangement of graphitic rings in the walls, carbon nanotubes can exhibit interesting electronic properties, attractive for potential applications in areas as diverse as sensors, actuators, molecular transistors, electron emitters, and conductive fillers for polymers. In order to meet specific requirements demanded for particular applications (e.g. biocompatibility for nanotube biosensors and interfacial strength for blending with polymers), chemical modification of carbon nanotubes is essential. Furthermore, carbon nanotubes of different properties may need to be covalently or non-covalently linked into various active components for device applications. Various covalent and non-covalent chemistries have been devised for making sophisticated carbon nanotube materials of good bulk and surface properties as demanded for specific applications. The tips of carbon nanotubes have been demonstrated to be more reactive than sidewalls, and hence a variety of chemical reagents have been attached at the nanotube tips. Recently, some interesting reactions have also been devised for chemical modification of both the inner and outer nanotube walls. Judicious application of these site-selective reactions to non-aligned and aligned carbon nanotubes has opened up the rich field of carbon nanotube chemistry. With so many covalent and non-covalent methods already reported, and more to be developed, the possibility of producing various functionalized carbon nanotubes of exotic physicochemical properties suitable for a wide range of practical applications will soon be in sight. Continued research in chemistry of carbon nanotubes should overcome some of the major hurdles that carbon nanotubes are facing in the race to the technological marketplace.

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