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The chemistry and application of carbon nanotubes

E G Rakov

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Abstract. The review concerns the main chemical and physicochemical properties and the methods of modification of carbon nanotubes, a novel promising material. The feasible and potential fields of applications of carbon nanotubes are outlined. The bibliography includes 573 references.

I. Introduction

Nanotubes (nanotubulenes, hereafter NTs) were discovered by Iijima in 1991.[1] A decade has passed since then; however, solid state chemists and physicists as well as materials scientists persist in giving increasing attention to NTs.[2] Moreover, it is NTs that are believed to be a tool for passage from macromolecules to nanotechnology and for transformation of the latter from a scientific concept into reality.

Currently, we cannot say whether these dreams will come true or not. Intensive research into NTs continues to expand, the number of publications increases rapidly;[3] some monographs, books of collected works and a textbook on NTs have been published.[4–10] Unfortunately, only a few out of the dozens of journal reviews concerning NTs were reported in the journals published in the Russian Federation.[11–16] In addition, at present these reviews fail to cover not only some recent advances, but also entire avenues of research into NTs. The author of this review strove to bridge this gap.

The background of the NT problem was briefly outlined recently.[15,16] The structure, some physical properties and methods for the preparation of NTs have also been reviewed.[14,16] To get acquainted with carbon NTs, we can also recommend a visit to the Website of the Michigan State University (USA) at URL http://www.pa.msu.edu/cmp/csc/nanotube.html. Here, it will only be remembered that perfect, defect-free NTs are formed by rolling planar atomic graphite sheets (graphenes) into seamless cylinders. Nanotubes can be multi-walled (MWNTs), comprising several coaxial cylinders, or single-walled (SWNTs). As a rule, the proportion of defects in SWNTs is less than in MWNTs. Moreover, SWNTs can become defect-free after high-temperature annealing in inert media. The structure of NTs affects their electronic, mechanical and chemical properties; because of this, SWNTs and MWNTs behave in fundamentally different manners.

The inner diameters of NTs vary between 0.4 nm and several nanometres. The volume of the inner cavity of NTs is sufficient for the molecules of other substances to occupy the cavity.

Graphene sheets in SWNTs and in each shell of MWNTs can have different orientations of the primitive graphene lattice vectors. This affects the properties of NTs.

The as-prepared NTs are usually closed by hemispherical or conical 'caps' at their ends.

A salient feature of NTs is their aggregation into rather stable bundles (bunches or ropes), which can be either bent or even closed (ring-like structures). The axes of individual NTs in the bundles are parallel to one another. The shortest distance between individual NTs is $\sim$0.32 nm. Nanotube bundles arise due to van der Waals forces. The intertubular space can be filled with 'guest' molecules.

Initially, most of NTs were synthesised by the arc method which involves graphite vaporisation in a dc arc struck between graphite electrodes in an inert gas flow. This technique was replaced by laser-induced thermal synthesis. This technique involves vaporisation of a graphite target under the action of a scanning laser beam in a furnace heated to a particular temperature and has a higher performance. In recent years, increasing attention has been given to pyrolytic synthesis from gaseous hydrocarbons (CH_4, C_2H_2, *etc.*) and CO. Preference is given to the catalytic processes which allow the preparation of not only MWNTs, but also SWNTs in relatively high yields.[16] It is thought that the processes proceeding in the presence of a 'volatile catalyst' introduced into the reaction zone in the form of vapours along with the substances to be decomposed can provide the highest performance.

Nanotubes can be prepared in different forms. Synthesis of NTs can give a tough precipitate of different density, *e.g.*, a rubber-like material consisting of entangled NTs (compact 'nanopaper', 'buckypaper', 'mats'), a web-like material and a textured material comprised of arrays of aligned NTs separated by some distance from one another (nanotube 'forest', nanotube 'towers').

E G Rakov D I Mendeleev Russian University of Chemical Technology, Miusskaya pl. 9, 125047 Moscow, Russian Federation.
Fax (7-095) 490 75 23. Tel. (7-095) 948 54 67. E-mail: rakov@rctu.ru

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In addition to hollow cylindrical NTs, conical, helical, horn-like ('nanohorns'), bamboo-like (consisting of individual closed extended sections), different types of alternating conical NTs ('nanobells' and 'fishbone') as well as L-, T- and Y-shaped NTs (both bent and branched) can also be formed.

The synthesis of NTs is often accompanied by the formation of other forms of carbon (*e.g.*, fullerenes, polyhedral particles and amorphous carbon). Therefore, in many instances purification of NTs (removal of side products) is a necessary stage.

Before going to the main body of the text, mention should be made of the term 'carbon nanotube chemistry', which is currently used in a rather broad sense.† Carbon nanotube chemistry covers, first of all, the synthesis and purification of carbon nanotubes and their opening in reactions with various oxidants. In addition, the subject matters of carbon nanotube chemistry are modification of NTs (filling the inner cavity with different reactants, attachment of functional groups to the NT ends and side walls and decoration of these surfaces with particular molecules, replacement of some of the carbon atoms on the NT side walls by atoms of other elements, insertion of 'guest' atoms and molecules into the intertubular space of NT bundles); the use of carbon NTs for template synthesis of nanowires, nanorods and nanotubes made of other substances; adsorption of gases on NTs and NT bundles and physicochemical properties of NTs. Research in the field of carbon nanotube chemistry also includes studies on the effect of the chemical modification on the electronic, magnetic, mechanical and other properties of NTs.

With rare exceptions, in this review we will not dwell on the methods for the preparation and purification of NTs and filling their inner cavities. These problems have been considered in detail recently.[16]

Chemical transformations of fullerenes, graphite and NTs exhibit some common features. Nevertheless, it should be emphasised that nanotube chemistry differs essentially from both fullerene and graphite chemistry. This is due to the unique shape, structural peculiarities and small diameter of NTs. Nanotubes differ from fullerenes in the relatively large volume of the inner cavity (stable fullerene molecules are too small to contain more than three or four atoms of other elements within the inner cavity). Perfect (defect-free) NTs differ from graphite in very low percentage or even the absence of chemically active dangling bonds. A feature of NTs is a variety of specific distances that are due to van der Waals forces (*e.g.*, the separations between individual shells of MWNTs, between individual tubules in NT bundles, *etc.*).

Each fullerene can be considered as a molecule which can form or be a constituent of molecular crystals. Graphite represents a typical layered polymeric crystal. In contrast to them, individual NTs cannot be thought of as individual molecules (SWNTs resemble molecules, while MWNTs are similar to carbon fibres) and NT bundles cannot be classified as conventional three-dimensional crystals (topologically, individual NTs and NT bundles represent one-dimensional and two-dimensional crystals, respectively.[18]).

Graphite, NTs and fullerenes can form intercalation compounds with fundamentally different structures. Graphite forms two-dimensional structures, NTs usually form one-dimensional structures (formation of two-dimensional structures is possible for the rolled-up NTs), whereas fullerenes form [topologically] zero-dimensional structures. In addition, only NTs can form several types of intercalation compounds with different geometries.

Sometimes, NTs exhibit quite unexpected chemical behaviour. For instance, bent NTs contain topological defects (*e.g.*, pairs of carbon pentagons and heptagons) and their reactivity differs from that of straight NTs. Carbon NTs also allow one to study the effect of the radius of curvature of the surface on the strength of the bonding between the substances reacting on the NT surface and the carbon atoms.

Modification of NTs can lead to essential changes in their electronic structure and functional properties and to creation of novel materials including those with unbelievable properties. The possibility of modification of fullerenes and NTs was first predicted theoretically (see, *e.g.*, Refs 19 and 20) and then confirmed experimentally.

This review concerns the chemical properties of NTs and their role in the processes of fabrication of the NT-derived end products. In the largest part of the review (Section VIII), we consider the potential fields of application of NTs. This seems to be of great importance since NTs are no longer 'exotic fruits'.

II. Filling of the inner cavities of carbon nanotubes

The inner cavities of NTs can be filled in the course of synthetic procedures or in a targeted manner after the preparation and purification of NTs. The latter strategy was found to be more versatile and rational.

Targeted filling can be performed with melts, solutions or reactive gases that are either involved in the chemical vapour deposition reactions or form covalent chemical bonds with carbon atoms within the NTs. Filling the NT cavities with gases due to adsorption represents a special case.

1. Nanotube filling in the course of synthetic procedures

Many substances can fill the inner cavities of NTs in the course of synthetic procedures.[16] In this review, we will dwell on the results reported in some of the most recent reviews and original studies.

According to Seraphin,[21] in the case of arc synthesis of NTs the additives (B, Mg, Mn, Fe, Co, Ni, Cu, Y, Nb, Mo and Ta) can be encapsulated into the NTs in the form of carbides. The filling of NTs with Nb, Ta and Mo carbides has been studied in more detail.[22] Nanotubes can also be filled with rare-earth element carbides and, in an H_2 atmosphere, with metallic Cu and Ge which do not tend to form carbides.

Two types of NT filling, a complete and incomplete one, have been described.[23] For instance, Se, Sb, S and Ge fill NTs completely (up to several micrometres long), whereas Bi, B, Al and Te form short particles. No rationalisation was provided to this phenomenon.

Sulfur is thought to play the key role in the formation of filled NTs in arc synthesis.[24] Thorough removal of sulfur from the anodic material reduces the probability of the growth of filled NTs.

The effect of sulfur on the NT growth mechanism in the case of arc synthesis was confirmed by Demoncy *et al.*[25] who found that sulfur added to the anode material favours the filling of NTs with such metals as Co, Ni, Cr and Dy if the content of S is less than 1% of the metal mass.

Boron, a well-known graphitisation catalyst, also has a strong effect on the NT growth mechanism.[26] A theoretical study of the effect of boron on the growth rate and morphology of NTs showed that boron stabilises the zigzag-shaped end of a NT, thus preventing it from 'capping' and favouring the NT filling.[27]

Other substances also can act as promoters. The addition of both a catalyst (2% Co) and promoter (5% Bi) to the anode material (graphite) resulted in an increase in the diameter of the grown SWNTs, namely, nearly 50% of them were found to be 1.5 nm and more in diameter and a large proportion of the SWNTs had a diameter of 2 nm.[28]

It seems to be more interesting to consider the growth of NTs with encapsulated fullerene molecules. In this case, the encapsulated fullerene molecules must affect the properties of composites filled with such NTs, the electronic properties of the NTs and their filling with other substances. Smith *et al.*[29] showed that the molecules of C_{60} and C_{70} and elongated capsules with diameters close to that of C_{60} can exist within NTs. It was also found that the

† This term was first used by the researchers from the Oxford University in 1996.[17] Their communication concerned the synthesis, opening (removal of 'caps'), filling and potential uses of NTs.

encapsulated fullerene molecules can move jumpwise and form pairs.

The assumption of the possibility of filling the NT cavity with C_{60} molecules was first proposed in the study of the products of laser-induced thermal synthesis.[30] After a short time, an experimental confirmation of this hypothesis was obtained, *viz*., nanoscale 'peapod' structures were found among acid treated and *in vacuo* annealed (1100 °C) reaction products.[31] Most of such structures have a NT diameter of 1.4 nm, which is twice as large as that of the C_{60} molecule (0.7 nm). They are characterised by yet another, third, type of specific separation that is due to the van der Waals forces (the above-mentioned two types are characteristic of MWNTs and NT bundles,[32] see also Section I). This separation differs from the interlayer spacing in graphite but is close to this value (the shortest distance between the C_{60} molecule and the NT wall is ~0.35 nm). The fact that the C_{60} molecules form pairs indicates that some other interactions occur in these systems in addition to the van der Waals forces.

Two-walled NTs with the inner diameter equal to that of the C_{60} molecule were found to be less abundant than SWNTs.[29]

It was assumed that C_{60} molecules are formed in the gas phase independently of NTs and enter the NT cavities most likely through defects due to diffusion that occurs in the gas phase (or, which is less probably, due to the diffusion over the NT surface) in the course of *in vacuo* annealing.[33] Then, the defects are 'healed' and the C_{60} molecules self-assemble into chains up to 30 units long and coalesce into interior tubes at temperatures above 1100 °C. There is an optimum temperature for the C_{60} molecules adsorbed on the outer surface to pass inside the NTs. At low temperatures, the saturated vapour pressure of C_{60} is too low and filling the NT cavity takes a long time. At high temperatures, the saturated vapour pressure is, on the contrary, too high and the desorbed fullerene molecules move away from the NTs.

The formation of interior elongated (several nanometres long) capsules was also explained by coalescence of the C_{60} encapsulated within NTs due to electron irradiation. The electron beam also damages the outer NT shell; however, this occurs at a lower rate than the inner coalescence.[34]

To prove that NTs are filed with C_{60} molecules, the NT walls were acid etched and the 'peads' were suspended in toluene.[35] The results of spectral studies of the suspension showed that the sample under study was characterised by a C_{60}-filled tube length fraction of 4.5%. The 'peapod' structures were found to be stable to at least 1200 °C (*cf*. 1000 °C for the transformation of pure cubic solid C_{60} into amorphous carbon).

Initially, it was assumed that nanoscale 'peapods' are solely comprised of NTs 1.3 to 1.4 nm in diameter and C_{60} molecules. More recently, this opinion was rejected. The C_{60} fullerene molecules can also be encapsulated within SWNTs obtained by arc method.[36] In this case, molecular fullerenes were found to be present inside 5% to 10% of all of the observed NTs and to have different chemical compositions spanning the range from C_{36} to C_{120} (C_{60} was the most abundant). A clear correlation was also found between the NT diameter and the encapsulated fullerene size.

Blockage of the filling of fullerene-containing NTs with other substances was observed.[36]

The inner cavities of NTs can be filled with carbides using not only the arc method, but also laser-induced thermal synthesis. The addition of boron to the material of graphite target resulted in the appearance of carbide particles inside the grown NTs near their ends.[37] Filling of NTs also seems not to be improbable in the case of catalytic pyrolysis of hydrocarbons (see, *e.g*., Ref. 38).

2. 'Targeted' filling of carbon nanotubes

Filling pre-fabricated NTs requires that they be opened (in other words, 'caps' at the NT ends should be removed). Most often, this can be done by selective oxidation, which, therefore, is a necessary stage of the process of 'targeted' filling of NTs.

a. Oxidation of carbon nanotubes

'Caps' at the ends of closed NTs are built of carbon pentagons and hexagons. The former type of polygon is more reactive, which determines the possibility of its selective oxidation. This can be achieved by using gaseous reactants, aqueous solutions or melts. Processes in solutions and melts can be initiated or activated electrochemically. Reactions in gaseous media are sometimes initiated using electric discharge or laser irradiation.

It should be kept in mind that NTs prepared *via* different synthetic routes can exhibit different behaviours in oxidation and other chemical reactions. For instance, the densities of materials produced by electric arc method and by laser-induced thermal synthesis can differ by an order of magnitude. Multi-walled NTs and SWNTs also behave in different manner, the latter being oxidised more readily.

Air, oxygen, CO_2 and oxygen plasma represent conventionally used gaseous oxidants. According to *ab initio* calculations,[39] the oxygen atoms bound to the carbon atoms at the end of an open NT cause its stabilisation. However, the authors of this study [39] believe that the heat of desorption of the CO_2 molecules changes its sign as the NT radius increases, so that an endothermic process is transformed into an exothermic one. Therefore, NTs with relatively large diameters are more prone to 'capping'. An increase in temperature also favours the formation of closed NTs. According to calculations, the oxidation energies of 'caps' and lateral surfaces of NTs differ appreciably.

The oxidation of a SWNT material containing carbonaceous impurities, Ni and Co begins at ~370 °C (Fig. 1), a large fraction of NTs being oxidised along with other forms of carbon at relatively low temperatures [40] {see also information posted at the website of the Rice University (USA) at URL [http://www.ruf.rice.edu/~johnz/researchorig.html]**D**}.‡ Exothermic oxidation of metals and amorphous carbon causes a local increase in temperature, which results in the oxidation of NTs at these 'hot spots'. Noteworthy is the coincidence of the curves shown in Fig. 1 *b* at temperatures above 450 °C. Probably, the conditions for preliminary oxidation in HNO_3 do not affect the amount of NTs consumed. (For unknown reasons, the curve *3* in Fig. 1 *a* and curve *2* in Fig. 1 *b* in the original study differ.)

Intercalation with $CuCl_2$ or Br_2 changes the character of the oxidation of MWNTs and allows their purification with O_2.[41–44] The interaction of Br_2 with unpurified NTs leads to intercalation of bromine molecules into graphite nanoparticles that are 'swelled' due to an increase in the interlayer spacings, which

‡ In most cases, the original research results posted at the Webpages cited in this review are represented in the form of abstracts or in other popular forms. Detailed information can be obtained by visiting the Websites labelled as **D**.

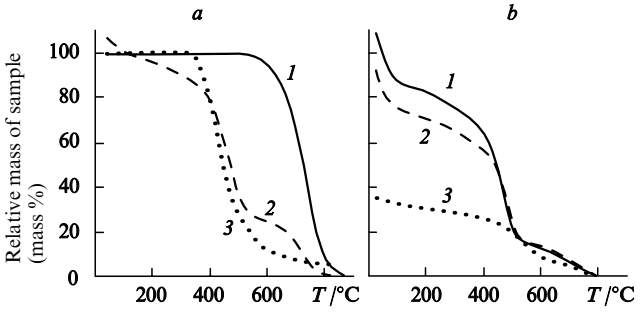
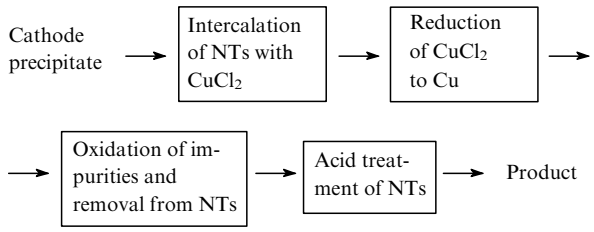


Figure 1. TGA curves for the oxidation of 1–2 mg NT samples in air.[40] The air flow rate was 100 cm^3 min^{-1} and the temperature was raised at a rate of 5 K min^{-1}. The data for the refluxed material was normalised to 100% at 100 °C to compare dry weights; (*a*): purified NTs (*1*), unpurified NTs (*2*) and NTs after a 16 h reflux in 3 M HNO_3 (*3*); (*b*): NTs after a reflux in 3 M HNO_3 for 4 (*1*), 16 (*2*) and 48 h (*3*).

favours a more ready oxidation of the nanoparticles. The reaction with Br_2 is completed after 96 to 240 h while the oxidation (4% O_2 in He, 530 °C) takes a period of 48 to 72 h.[42] The yield of purified NTs is determined by the O_2 flow rate, the sample mass and the conditions for arc synthesis and can reach a value between 10% and 20%. Some of the Br_2 molecules form complexes with the carbon atoms of the NT walls.

Purification of NTs using $CuCl_2$ is carried out as follows:



This procedure is inapplicable to SWNTs since the yield of the pure product obtained using the Br_2-O_2 system is very low (only ~3%). This is thought to be related to different curvatures of the MWNT and SWNT surfaces.[45]

Functionalisation of SWNTs reduces the rate of their oxidation. Zimmerman *et al.*[45] studied purification of NTs with moist chlorine and proposed a mechanism which involves the formation of hydroxy- and chloride-functionalised NT 'caps' with the $\rangle C-Cl$ and $\rangle C-OH$ groups that withstand further oxidation. The description of the experimental setup and material of a discussion concerning the purification mechanism can be obtained *via* the Internet [URL http://www.ruf.rice.edu/~johnz/researchorig.html]**D**.

Smith and Luzzi[46] reported the 'closure' of NT ends in inert atmosphere at a very low temperature (~550 °C). This is consistent with the idea of the 'closure' of dangling bonds at the open NT ends in O_2, Cl_2 or H_2 atmospheres.

The selectivity of impurity oxidation in the course of purification of SWNT bundles in a 1% O_2-Ar mixture can be enhanced by using catalysts, *e.g.*, ultrafine gold particles with a diameter of ~20 nm, and benzalkonium chloride as surfactant.[47] (The article contains no information on whether or not the NT opening occurs in the low-temperature oxidation at 350 °C.) After a short time the oxidation conditions were refined and the optimum concentrations were found to be 0.6 at.% for gold particles and 7 g litre^{-1} for benzalkonium chloride.[48] It was also shown that amorphous carbon burns out in the temperature range from 300 to 550 °C, the NT oxidation temperatures span the range from 550 to 750 °C and the residual graphite flakes are oxidised at temperatures above 730 °C. It was suggested that benzalkonium chloride facilitates breakdown of NT bundles.

The list of reactants that can be used in the form of melts is also short. Opening of 'capped' NTs was carried out in air using molten lead at 400 °C (the lead oxide that is formed in the course of the reaction acts as a catalyst).[49,50] The reaction in the presence of molten bismuth in air at 850 °C follows the same pattern (in this case, Bi is oxidised into Bi_2O_3). Experiments on NT opening can also be performed with V_2O_5 (see Ref. 51) and low-melting metal nitrates (see below).

Aqueous solutions were found to be the most appropriate and efficient reagents for NT opening. High yields of open NTs can be achieved by prolonged refluxing of NTs in HNO_3. The efficiency of aqueous solutions of other reagents (*e.g.*, $K_2Cr_2O_7$, $KMnO_4$, H_2O_2, OsO_4, RuO_4, $HClO_4$, H_3IO_5) and various mixtures was also studied. It was shown that treatment with concentrated hydrochloric acid can lead to the opening of NTs.[52] Relatively high yield of the open purified NTs obtained by pyrolytic technique was achieved using a $KMnO_4$ solution in H_2SO_4.[53,54] Experiments with $H_2SO_4-HNO_3$ mixtures were also reported.[55]

The mechanism of the interaction between various oxidants and NTs remains unclear as yet. It is known that NT shells with different chiralities are oxidised at different rates.[56]

Studies on the NT oxidation in the course of their purification were reviewed by Duesberg *et al.*[57]. They pointed out that the results obtained by different authors who used nitric acid treatment of NTs are close despite considerable differences in duration of the acid treatment, the concentration of nitric acid and the operating temperatures. After oxidation, acid-treated NTs are covered by small fragments of carbon particles which should be washed off with alkali solutions. Duesberg *et al.*[57] also described mechanical and physicochemical methods for purification of NTs.

b. Filling of carbon nanotubes from liquid media

General methods of filling carbon NTs from liquid media can be conventionally divided into three groups. These are one-step, two-step and three-step methods. The one-step method uses the interaction of NTs with metal nitrates in the course of nitric acid assisted opening of NTs. Subsequent removal of HNO_3 and thermal decomposition of the nitrates upon calcination of NTs leads to the formation of metal oxide crystallites inside the NTs.[17,58]

The two-step method involves the interaction of pre-opened NTs with concentrated salt solutions. Preference should be given to this method in those cases where fillers are unstable or poorly soluble in acid.[58]

The three-step method involves an intermediate stage between the opening and filling of NTs, namely, *in vacuo* annealing at 2000–2100 °C.[59,60]

Surface tension is an important characteristic of liquids that fill NTs. Only those substances can be soaked in the NT cavities that have a surface tension of at most 150 mN m^{-1} (see Ref. 61). On the other hand, this numerical value is a function of the NT diameter. For instance, the action of capillary forces allows the filling of NTs with a diameter of at least 4 nm for $AgNO_3$ [61] and ~1 nm for PbO and V_2O_5.

In air, NTs can also be filled with PbO_2; *e.g.*, a nanorod with a diameter of 4 nm and a length of more than 400 nm was obtained at 450 °C.[59] Molten V_2O_5, Bi_2O_3, B_2O_3 and MoO_3 also fill the inner cavities of NTs with ease to form continuous crystals along the entire nanotube length.[51,62] If the NT diameter is less than 3 nm, a disordered glassy phase is formed instead of the crystalline phase for unknown reasons.

Filling of SWNTs with a diameter of at most 3.5 nm with bismuth occurs upon heating of mixtures of capped NTs with the metal nanoparticles to 400 °C in air.[28,63] The stability of the filled NTs under conditions of electron irradiation in vacuum was studied.[64]

Kiang *et al.*[63] reported a study on the NT filling with bismuth (i) in the course of the arc synthesis of NTs (equal amounts of Bi and Co were introduced into the graphite anode material), (ii) from melt or vapours (a mixture of NTs and Bi was heated in air) and (iii) from aqueous solutions [boiling in 1 M solution of $Bi(NO_3)_3$ in HNO_3 followed by reduction with H_2]. The abundance of filled NTs was found to be less than 1% for method (i), ~10% for method (ii) and more than 30% for method (iii) provided that the experiments were performed with the same type of NTs.

Since only a few low-melting metal oxides are known, recent studies were carried out using metal halides and nitrates. In particular, NTs were 'doped' with $ZrCl_4$, UCl_4, AgCl, $CdCl_2$, CsCl, AgBr, with AgCl–AgBr mixture and with eutectic mixtures $KCl-UCl_4$ and $KCl-ThCl_4$.[36,65,66] Filling with uranium tetrachloride was found to occur only in the presence of KCl, since the surface tension of UCl_4 exceeds 370 mN m^{-1} at 900 K. At temperatures above the liquidus temperature, the mixtures with the molar ratios $KCl:UCl_4 = 1:1$ and 2 : 1 are characterised by a surface tension of 120 (750 K) and 68 mN m^{-1} (950 K), respectively. The surface tension of silver chloride is 173 mN m^{-1} (833 K) while that of silver bromide is 151 mN m^{-1} (800 K).

The structure of the metal halide 'dopant' affects the crystal chemistry features of the product (for detailed information, we recommend visiting the Website at URL http://www.cpes/sussex.

ac.uk/nanotec99/present/mlhg.htm). For instance, depending on the NT structure, layered $CdCl_2$ and CdI_2 encapsulated in NTs were found in different polymorphous modifications. Substances that form chain structures can either retain native polyhedral chain patterns ($ZrCl_4$, NbI_4) or change them inside NTs. Bulky chain halides ($ThCl_4$, UCl_4) form one-dimensional structures inside NTs.

A 0.1 nm space resolution study of the structure of an ultrasmall single crystal, a KI inclusion into a SWNT, obtained by heating open NTs with molten salt revealed considerable lattice distortion as compared to bulk crystals.[67–69] The cross-section of the KI crystal encapsulated within a 1.6-nm-diameter NT represented a 3×3 atomic array. A longitudinal contraction of the KI crystal by 0.695–0.705 nm along the $\langle 001 \rangle$ axis as compared to the 'bulk' substance was determined. The coordination numbers (CN) of the face and edge atoms were found to be 5 and 4, respectively. Since the proportion of such atoms is rather large, one can expect that differences in the geometry and CN will affect the electronic properties of substances. For instance, typical metals can turn into dielectrics or *vice versa*. This opens up possibilities for the design of new materials.

Even smaller KI single crystal was obtained in an 1.4 nm-diameter NT. The cross-section of this crystal represented a 2×2 atomic array. Each atom was found to have a CN of 4.[68] Compared to the bulk phase, a strong tetrahedral distortion of the cubic crystal lattice was observed and the lattice parameter was found to be more than halved. As in the preceding case, the $\langle 001 \rangle$ direction was parallel to the NT axis.

Lattice distortions and changes in the crystal lattice parameters of the substances encapsulated within NTs were also observed by other authors (see, *e.g.*, Ref. 63); however, detailed study and discussion concerning the prospects for practical implementation of this phenomenon were first undertaken.[67]

Silver, cobalt and copper nitrates have low melting temperatures and their melts are characterised by low surface tension. They are oxidants and can therefore be encapsulated into capped NTs. These compounds were used for the preparation of NTs with encapsulated continuous silver rods 4 nm in diameter and up to 47 nm in length and CoO rods 1.7 nm in diameter and 17 nm long.[59]

Govindaraj *et al.*[70] used metal halide hydrates (in particular $HAuCl_4 \cdot x\,H_2O$) as the reactants for filling open SWNTs and reported the conditions for filling NTs with molten $PdCl_2$.

β-Tin nanowires were obtained by electrolysis of a $LiCl-SnCl_2$ melt using graphite electrodes.[22]

Electrochemical preparation of Sn–Pb nanowires 40 to 90 nm long inside NTs was reported.[71]

Usually, nanowires are 1.0 to 1.4 nm in diameter and up to 90 nm long. In some cases, it has been possible to prepare single-crystalline metal nanowires; however, most often they represent polycrystalline structures.[70] Sometimes, filling of NTs was accompanied by their decoration due to insertion of the metal atoms into the intertubular space of NT bundles.[70] The thickness of the intercalated metal layers was 0.4 to 0.5 nm, which is somewhat larger than the van der Waals separation between individual NTs ($\sim$0.3 nm).

Most often, carbon NTs are filled using aqueous solutions[17] since this method is easy to operate.

The substances encapsulated into NTs can participate in chemical reactions. These are, *e.g.*, thermal decomposition of nitrates resulting in the formation of oxides or metals; reduction of metal chlorides and oxides with hydrogen to obtain NTs filled with Cu,[41] Ni, Fe, Ag, Au, Pd and Rh (see Ref. 58); reactions between chlorides and dioxygen to prepare NTs with encapsulated uranium oxychlorides[65]) and alkali hydrolysis of $SnCl_2$. Kyotani *et al.*[72] studied the filling of carbon NTs with the acid $H_2PtCl_6 \cdot 6\,H_2O$ in solution and reduction of the acid by $NaBH_4$ at room temperature. Sulfidising reactions of NTs with encapsulated CdO or $AuCl_3$ in an H_2S atmosphere to give CdS and AuS_x were investigated.[58] It was found that many substances encapsulated into NTs can be dissolved in HNO_3. Decomposition of silver chloride and silver bromide encapsulated within NTs and then exposed to light or electron beam has been reported.

To prepare NTs with encapsulated SnO, they were opened, washed with HNO_3, placed in a concentrated $SnCl_2$ solution and then the pH value of the suspension was slowly increased to 10.2 using a solution of Na_2CO_3.[73] Encapsulated crystallites were found to have a spherical or ellipsoidal shape and a diameter from 2 to 6 nm.

Successful synthesis[74] of MWNTs with extremely small inner diameter (0.4 nm) opens up the prospects for the preparation of nanowires with uniquely small diameter by encapsulation into such NTs.

c. Filling of carbon nanotubes from gaseous media

Filling the inner cavity of NTs using chemical vapour deposition technique can be performed using, *e.g.*, volatile metal compounds which can decompose on heating to give non-volatile substances. Using this method and $Fe(C_5H_5)_2$, the inner cavities of the NTs grown in the pores of anodised aluminum (Fig. 2) were filled with Fe or Fe_3O_4 nanoparticles.[75] The formation of the oxide inside NTs in the decomposition of ferrocene was explained by partial oxidation of the iron.

A similar process was performed using $Ni(C_5H_5)_2$ at 275 °C.[76] Carbon NTs with the outer diameter of 30 nm were found to be filled with Ni wires 4 nm in diameter and up to 500 nm long. It is noteworthy that no nanowires were formed near the open ends of the NTs; this can hardly be rationalised. It is also unclear why the diameter of the nickel nanowires appeared to be much smaller than the inner diameter of the carbon NTs. Usually, the diameters of the nanowires prepared using other methods were only slightly different from the inner NT diameter (see, *e.g.*, Refs 23 and 50).

Filling of NTs with various compounds was studied by the molecular dynamics method. Simulation was performed assuming that filling occurs due to the capillary forces and that the model NT 2.74 Å in diameter comprised 56 carbon atoms. According to calculations, lead clusters can fill NTs along their entire length, whereas carbon and sulfur clusters are retained near the open ends of the NTs.[77] Carbon NTs can also be filled with molten selenium which forms atomic chains.[78]

Targeted filling without pre-opening the NTs occurs in the course of catalytic pyrolysis of hydrocarbons in porous $AlPO_4$.[79] The porous material is preliminarily filled with cobalt which is then encapsulated into NTs. Experiments with NaY zeolite template also revealed the formation of NTs; however, no filling of the NTs with the catalyst particles was observed due to different character of the interaction between the catalyst and template.

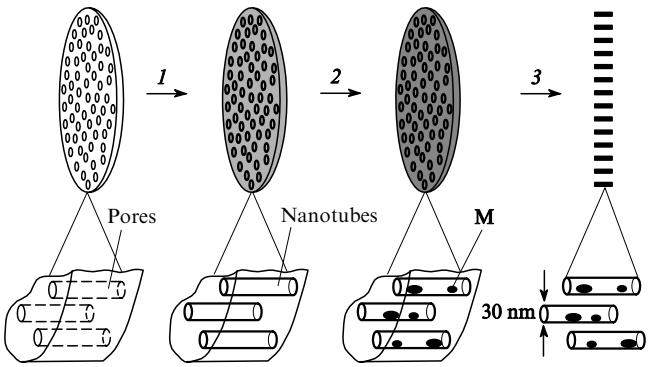


Figure 2. A scheme illustrating the filling of NTs from the gas phase using a porous Al_2O_3 film.[75]
Propylene pyrolysis (*1*), chemical vapour deposition of the metal (*2*) and dissolution of the template in NaOH (*3*). The metal particles are labelled as M.

A short review of recent advances in the field of the preparation of filled NTs and metallic nanowires was reported by Terrones *et al.*[80]

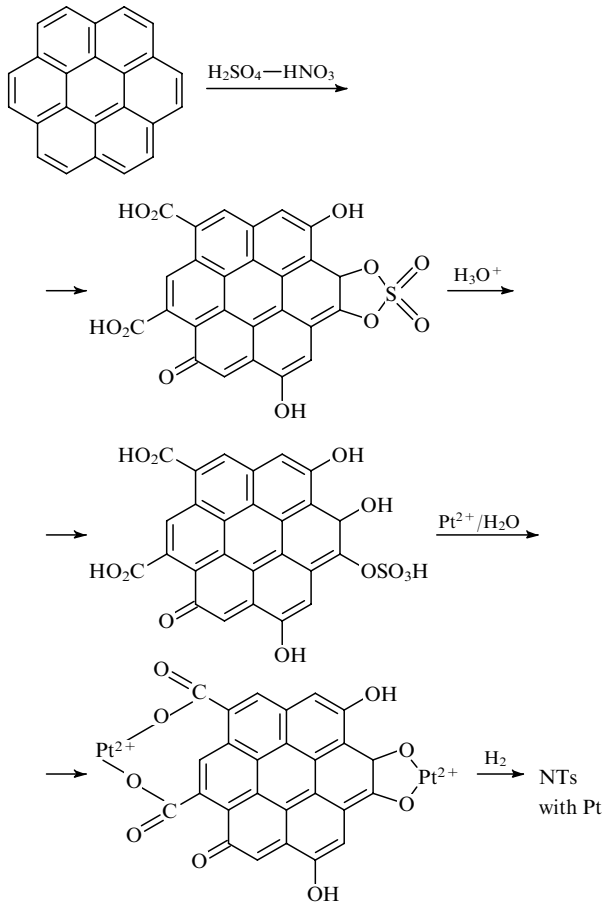
III. Functionalisation of carbon nanotubes

Chemical modification of activated carbons and carbon fibres has been studied in detail. Several methods for attachment of oxygen-containing groups to the NT surfaces have been developed.[81,82]

Cahill and Rohling[83] showed that functional groups can bound to the NT side walls. The oxidised surfaces of NTs were found to be covered by the carboxylic, carbonyl and hydroxyl groups in the approximate ratio 4 : 2 : 1.[53]

The behaviour of acid groups on the surfaces of nitric acid treated NTs was studied by temperature-programmed decomposition and acid-base titration.[84] The concentration of these groups on the NT surfaces was found to be $\sim 1 \times 10^{20}$ g^{-1}, whereas graphite treated under the same conditions showed a lower concentration (5.3×10^{19} g^{-1}). Sonication of NTs prior to the functionalisation in acids increases the concentration of acid groups.

Oxidation of NTs with a $H_2SO_4-HNO_3$ mixture leads to a higher concentration of functional groups on the surface than in the case of treatment with HNO_3.[85] The formation of functional groups and their subsequent bonding to the metal ions can be described by the following mechanism:



Prolonged acid treatment followed by heating in air is used for purification of SWNTs {see Ref. 40 and material posted at URL [http://www.ruf.rice.edu/~johnz/researchorig.html]**D**}. After a 16 h reflux in 3 M HNO_3 (120°C), washing and drying the mass loss was 18%, of which ~6% were identified as metal impurities. The surfaces of acid treated NTs were found to be uniformly coated with polyaromatic hydrocarbons, which can be removed by oxidation in air at 550 °C for 30 min. The residue (~20% of the initial mass) represented high-purity pristine SWNTs. The impurity content was at most 2%. Oxidation of these NTs begins at 735 °C. This temperature is ~125 °C higher than that reported earlier,[55] which indicates that the NTs are defect-free and contain no dangling bonds.

Long-term acid treatment of NTs leads to changes in the chemical composition of the material. Indeed, the uniform hydrophilic carbonaceous precipitate disappears and NTs randomly coated with both the precipitate 'spots' and particle aggregates appear in addition to the pristine NTs after 48 h with 3 M HNO_3. A large fraction of NTs was found to be damaged and shortened ('cut'). Being oxidised in air, this material behaves in a different manner compared to the material obtained after acid treatment for shorter times (see Fig. 1) and the yield of purified NTs becomes nearly halved.

It should be noted that SWNTs obtained by different methods exhibit different behaviour in the course of acid treatment and subsequent oxidation. Oxidation of nitric acid treated SWNTs with gases results in selective removal of thin NTs.[86]

Functional groups can be removed from the surface of NTs by heating. The process begins at temperatures above 623 K;[87] however, complete removal is observed at 1073 K (higher stability of functional groups up to a temperature of 1173 K was also reported[83]).

The density of oxidised (defect) carbon sites in closed (10,10)-NTs after acid treatment and removal of CO_2 and CO at 1273 K can be determined using ozone titration.[88] The fraction of defect carbon sites was estimated to be 5.5%.

To enhance the possibilities of atomic force microscopes (AFM) with nanotube probe tips, the tip ends are functionalised.[89–91] This can be done with both solutions[89–91] and gases.[92–94] The latter approach is thought to be preferred since it involves a single-step treatment.[92] A schematic representation of the AFM cantilever functionalisation process is shown in Fig. 3. The treatment procedure uses electric discharge in O_2, H_2, N_2 and H_2-N_2 mixtures. Modified probes can be used for studying the surfaces of non-ionisable self-assembled layers terminated in OH

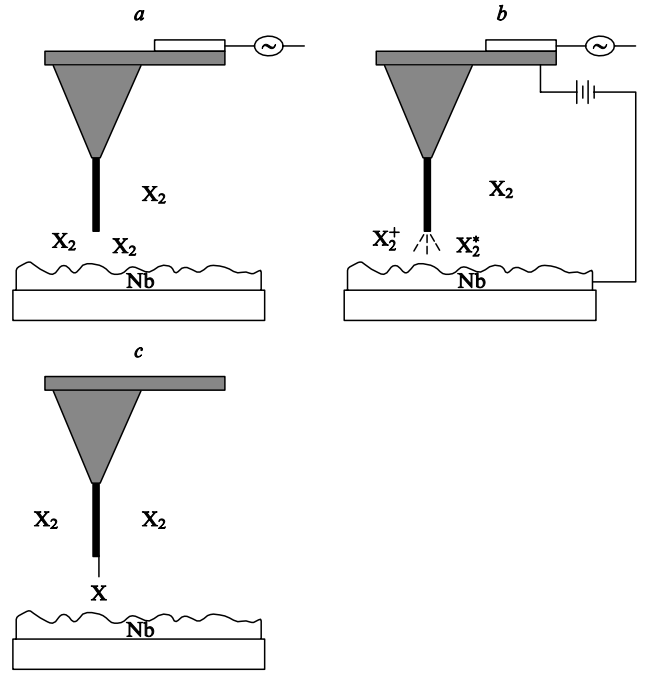


Figure 3. Schematic representation of the AFM cantilever functionalisation process.
Carbon nanotube attached to a cantilever is oscillated above a sputtered niobium surface in the presence of gas, X_2 (*a*); applying a potential produces electric discharge between the oscillating NT and the surface (*b*) and the nanotube probe tip functionalised with X (*c*).

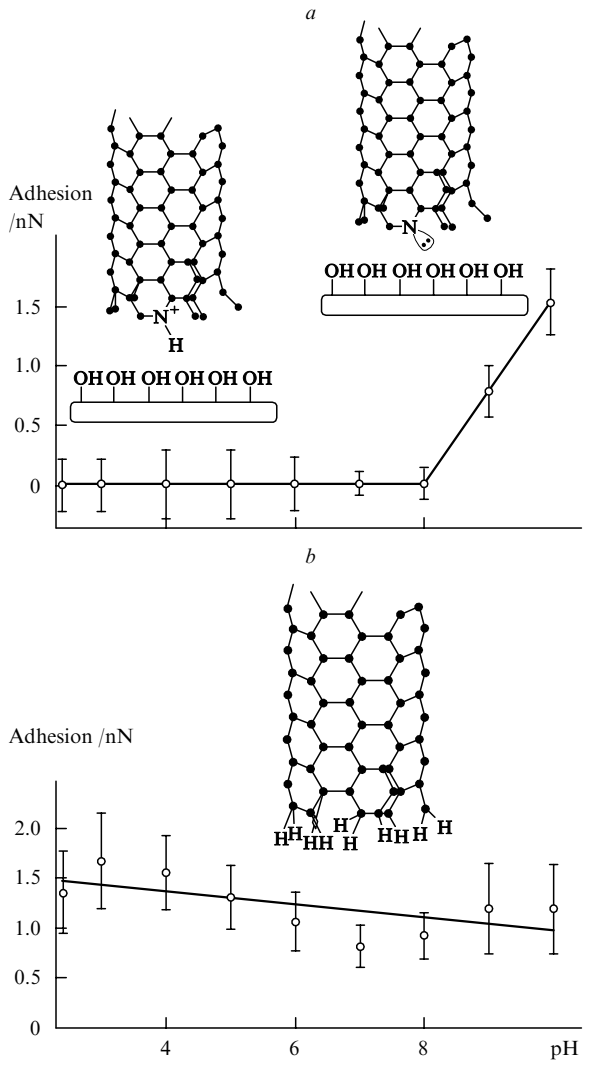


Figure 4. Adhesion of nanotubes to the surface of self-assembling monolayers as a function of pH (measured using an AFM).
A probe with a nanotube tip modified by nitrogen (*a*) and hydrogen (*b*) atoms.[92]

groups. Modification of nanotube tips using a discharge in N_2 atmosphere results in the formation of nitrogen-containing heterocycles at the tip ends. Chemically modified nanotube tips can be used for measuring the pH values of different surfaces (Fig. 4).

High degree of saturation of nanotube tips with functional groups (up to the atomic ratio O : C = 0.2) is achieved by treatment with a low-pressure ammonia plasma followed by oxidation with a $NaClO_3$ solution.[93]

According to calculations, bombardment of SWNT bundles with $CH_3^{\bullet}$ radicals with energies between 10 and 80 eV must result in bonding the radicals or their fragments to the surface.[94]

A theoretical study on the hypothetical structure of NTs 1 nm in diameter and 5 nm long with acid functionalities attached to the outer surface and on the structure of NTs linked through such functional groups has been reported.[95]

a. Fluorination of carbon nanotubes

Fluorination plays a distinctive role in the modification of NTs and functionalisation of NTs.

A review by Touhara and Okino [96] covers the latest studies of researchers from Japan in the field of fluorination of carbon materials. The authors of this review believe that fluorination belongs to the most efficient chemical methods of modification and control of the physicochemical properties of these materials. They constructed a binding energy scale for the C – F bonds and inferred that these bonds can be of different nature and can vary from covalent to semi-ionic and thus be responsible for the variety of properties of fluorinated materials.

Graphite fluorides and intercalation compounds based on them are known to be of paramount importance as compared to other graphite compounds (oxides and salts). They are readily available, exhibit relatively high chemical and thermal stability and are characterised by high energy content, which makes them the subject of great practical interest as promising materials for chemical current sources and components for solid lubricants. Studies on fluorination of NTs have led to some remarkable findings.

Pioneering experiments on the fluorination of MWNTs were carried out by researchers from Japan in 1996.[96,97] It was shown that fluorine is first of all intercalated into the outer layers of NTs. Fluorinated graphene sheets were found to retain their tubular structure on heating up to 300 – 400 °C, the spacing between them being increased to 0.53 and even to 0.65 nm at higher temperatures. As in the case of graphite, nanotube fluorination is accompanied by buckling of graphene sheets and the formation of a polymeric structure 2 to 3 nm thick with covalently bonded fluorine atoms on the surfaces of NTs. By analogy with fluorination of graphite, nanotube fluorination was assumed [97] to proceed as stepwise process. However, this hypothesis was not confirmed more recently.

Experiments on fluorination of MWNTs 20 to 40 μm in diameter and up to 10 μm long obtained by catalytic pyrolysis [98] showed that these NTs are more reactive than graphite but less reactive than C_{60} and C_{70}.[96] The reaction of the NTs with a $F_2 - HF - IF_5$ mixture at room temperature resulted in the formation of a black compound of composition $CF_{0.4}$ (fluorination of graphite under the same conditions resulted in graphite monofluoride). The reaction product was found to represent an intercalate, though no intercalation of IF_5 into the NTs was observed. The product retained the tubular morphology and sp^2-hybridisation of the carbon atoms.

Fluorination of NTs at 500 °C for 4 h resulted in distortion of a regular structure of NT bundles and in the formation of a white compound with a chemical composition close to that of graphite monofluoride (at 600 °C).

Studies of the electrochemical properties of fluorinated NTs [96,99] revealed that the capacity of a nanotube-derived electrode material fluorinated at 480 °C and then used in batteries can be as high as 620 A h kg^{-1}.[96]

The results of earlier studies [98,99] were to some extent confirmed by the results of experiments on the fluorination of 'buckypaper' fabricated from purified SWNTs with dilute F_2 (9% F_2 in He).[100] It was shown that fluorine atoms can be attached to the side walls of NTs.[100] The atomic ratio F : C was found to be merely ~0.1 at 150 °C, ranged between 0.46 and 0.52 at 250 °C and within nearly the same limits at 325 °C and corresponded to the formation of a compound with approximate composition C_2F, which retained its tubular structure. At temperatures above 500 °C most of the NTs were destroyed and the formation of structures similar to MWNTs was observed at 500 °C. Fluorination was found to have a strong effect on the electronic properties of NTs, namely, the untreated NTs were conductors while the fluorinated NTs were insulators.

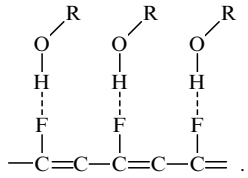
Surprisingly, fluorination of NTs at $T \leqslant 325$ °C appeared to be reversible. The interaction between fluorinated NTs with a composition close to C_2F and anhydrous hydrazine resulted in removal of the fluorine atoms and in recovery of the initial structure of the NTs. This was accompanied by recovery of many (but not all) initial properties of the NTs. This was associated [100] with the reaction

$$CF_{n\,(NTs)} + \frac{n}{4}\,N_2H_4 \longrightarrow C_{(NTs)} + n\,HF + \frac{n}{4}\,N_2\,.$$

However, no structure recovery was observed if NTs were fluorinated at 400 °C.

'Fluorocarbon' NTs were shown to react with such a strong nucleophile as sodium methoxide to give a relatively stable compound with an approximate composition $C_{4.4}F(OCH_3)_{0.25}$. Sonication of fluorinated NTs in various alcohols leads to solvation of the NTs, the degree of solvation being much higher than that reported by Chen *et al.*[102] Solvated NTs can form solutions, which is of great importance for the development of nanotube chemistry and some technological procedures, *e.g.*, for nanotube sizing and purification.

Mickelson *et al.*[101] studied the fluorination of thoroughly purified NTs primarily with the (10,10) structure. The reaction product consisted of ~70 at.% C and 30 at.% F and corresponded to the empirical formula $C_{2.33}F$. The C–F bond ionicity was found to be much higher than in, *e.g.*, alkyl fluorides. This allowed the preparation of metastable solutions of the NTs in methanol, ethanol, 2,2,2-trifluoroethanol, propan-2-ol, butan-2-ol, n-pentanol, n-hexanol, cyclohexanol and n-heptanol by sonication. These solutions were stable for 24–168 h. Of the solvents used, propan-2-ol and butan-2-ol were found to be the best. The solubility of NTs in butan-2-ol was at least 1 mg ml^{-1}. It was assumed that solvation is accompanied by the formation of hydrogen bonds following the scheme



Prolonged sonication of the fluorinated NTs (~10 min and longer) results in removal of some of the fluorine atoms from the surface of NTs.

The solutions of the NTs in chloroform appeared to be much less stable. Attempts at solvating the NTs in perfluorinated liquids, acetic acid and aqueous acetone solutions also failed.

Reactions in solutions also proved the role of hydrazine as defluorinating agent. The structures of the NTs precipitated out of the solution after adding anhydrous hydrazine and characterised by low fluorine content were only slightly different from those of the untreated NTs.

Smalley *et al.*[103] succeeded in replacing the fluorine atoms attached to the side walls of NTs by alkyl groups. Fluorinated NTs of stoichiometry $C_{2.33}F$ were treated with either a solution of alkyllithium in alkane or with Grignard reagents RMgBr (R = Me, Et, Bu, C_6H_{13}, C_8H_{17} or $C_{12}H_{25}$) in THF. The reactions were activated by sonication.

It was found that the NTs alkylated with hexyl groups can be dissolved in chloroform (up to a concentration of ~0.6 g $litre^{-1}$), THF (~0.4 g $litre^{-1}$) and methylene chloride (~0.3 g $litre^{-1}$). No flocculation was observed over a period of several weeks.

Heating of the alkylated NTs in air can lead to recovery of the initial composition the NTs had before fluorination. The hexylated NTs decompose or are oxidised at 250 °C. Judging from the mass loss over a period of 1 h, there are 10 carbon atoms of the outer surface of the NT per hexyl group.

Smalley *et al.*[103] also reported convincing proofs of the chemical nature of the bonding between alkyl groups and the surface of NTs. They also found that alkylated NTs can form true solutions and various complex functional nanostructures linked through the atoms attached to their side walls.

To establish the fluorination and functionalisation mechanisms, Kelly *et al.*[104] studied fluorinated and butylated NTs by scanning tunnelling microscopy (STM) and carried out quantum-chemical calculations of the energies of different isomers. The observed STM images were consistent with the formation of the 1,4-isomer (Fig. 5), though the calculations predict that this isomer is only slightly more stable than the 1,2-isomer. The

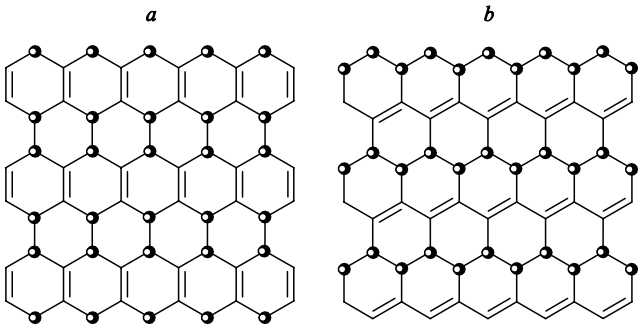


Figure 5. Structure of fluorinated nanotubes. 1,4-isomer (*a*) and 1,2-isomer (*b*).

mechanism of fluorination involves the addition of fluorine atoms to the side walls of NTs around the circumference of the NTs in the intermediate stages.

Fluorination of the external side walls of NTs affects their electronic properties. For instance the conductivity type of NTs can vary from semiconducting to metallic (and *vice versa*).[105]

The binding energies of one, two, three and four fluorine atoms to the side-wall carbon atoms of a (10,0)-NT have been calculated.[106] The sum of the binding energies of two fluorine atoms to the carbon atoms of the NT is much higher than the binding energy in the F_2 molecule.

A group of researchers from Japan studied the process of fluorination of the inner cavity of NTs and the effect of changes in the chemical composition of the NTs on their properties.[107] The starting material, open-end SWNTs, was produced in a porous Al_2O_3 template with a pore diameter of ~30 nm and a pore length of 75 μm. After treatment with F_2 under isothermal conditions at 50 to 200 °C and atmospheric pressure the template was dissolved to separate the fluorinated NTs (Fig. 6). The product was shown to retain the tubular structure.

Fluorinated carbon nanotube membranes are thought to be a perfect material for electrochemical batteries or capacitors.[96]

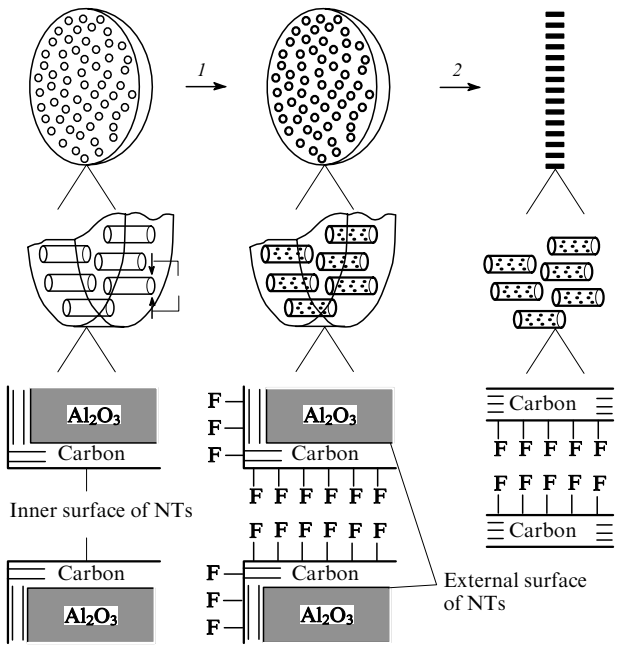


Figure 6. The preparation of nanotubes with fluorinated inner cavity using a porous Al_2O_3 film (deposition of the carbon layer is not shown).[107] Fluorination (*1*) and dissolution in HF (*2*).

Long-term (168 h) fluorination of MWNTs with 'roll' structure and nanoparticles obtained by arc method with BrF_3 vapours at room temperature results in tubular or quasi-spherical C_2F.[108] This is accompanied by corrugation of the external shells of the NTs while the inner shells of the NTs retain the shape of coaxial cylinders. As the depth of fluorination increases, the interlayer spacings and the NT diameter also increase. At a critical fluorination depth (or, in other words, at some critical strain), a number of the outer shells are simultaneously unrolled, thus leading to the formation of multilayered plate-like particles.

This phenomenon was first observed. The interlayer spacing for the untreated NTs was 0.342 nm (by 0.007 nm larger than for graphite), whereas that for the fluorinated NTs was 0.614 nm, which is indicative of a very weak interlayer coupling. However, the role of Br_2 used in the form of (i) vapours to pre-saturate the NTs and (ii) solution to evaporate BrF_3 is still to be clarified.

b. Soluble carbon nanotubes

The ability of NTs to dissolve in various solutions opens new possibilities for their purification, classification (selection of fractions with uniform structure and equal length) and modification.

Pioneering studies on the attachment of organic functional groups to NT bundles by radiation-induced photolabilisation using biradicals and nitrene sources followed by treatment with dichlorocarbene were carried out by Smalley *et al.*[109] They found that the interaction with dichlorocarbene leads to the appearance of chlorine within the NT bundles but failed to determine whether the reactant is attached to the NT walls or to amorphous carbon due to insufficient purity of the starting material. Dichlorocarbene was attached to the double bond of a NT using another reaction, namely, the interaction of NTs with $PhHgCCl_2Br$.[109] The reaction product was found to contain $\sim$2 at.% of chlorine.

Solvation of SWNTs due to the attachment of octadecyl groups has been reported.[102] Single-walled NTs with an average diameter of 1.38 nm were obtained by arc discharge technique, purified, cut to 100 to 300 nm, opened, acid-functionalised (in HCl in the final stage) and treated with $SOCl_2$ containing a small amount of DMF for 24 h at 70 °C. The solid phase was separated from the solution, washed with anhydrous THF, dried and heated with octadecylamine at 90–100 °C for 96 h. The solid residue obtained after removal of excess amine and four-fold washing with ethanol contained up to 60% of NTs that were extracted using a dichloromethane solution. It was found that the functionalised NTs can be dissolved in chloroform, benzene, toluene, chlorobenzene, dichlorobenzene and CS_2. The solubility limit in dichlorobenzene and CS_2 was greater than 1 g litre^{-1}. Dilute solutions were brown while nearly saturated solutions were black.

Functionalisation was accompanied by noticeable swelling of NTs, which was tentatively related to the breakdown of the NT bundles. It should be noted that a $\sim$300-nm (10,10)-NT contains $\sim$50 000 carbon atoms and has a molecular mass of $\sim$600 000 Da.

Solutions of solubilised SWNTs with attached $CONH(CH_2)_{17}CH_3$ groups were studied by IR, Raman and UV spectroscopy[102] and by the ^{1}H NMR (see Ref. 102) and ESR spectroscopy.[110] The ESR signal with the parameters $g = 2.003$ and $\Delta H = 2.1$ G observed by Chen *et al.*[110] is characteristic of the cut NTs. Reactions of NTs with Br_2 and I_2, which can also proceed in solutions, were shown to cause changes in the electronic structure of the NTs.

Dissolution of SWNTs *via* their functionalisation has been studied in detail.[111] The SWNTs were first treated with $SOCl_2$ and then the chloride groups were replaced by amino groups using the reaction with 4-$CH_3(CH_2)_{13}C_6H_4NH_2$. Solution-phase doping of the solubilised NTs with iodine and bromine resulted in pronounced changes in the vibrational spectra of the NTs and served as evidence that the reactions in the solutions do proceed. Compared to the cut NTs, the uncut functionalised NTs were found to be much less soluble. Distinctions between the absorption bands of semiconducting and metallic NTs and better solubility of the NTs of larger diameter (their fraction is small) in pyridine than in THF, CH_2Cl_2 and CS_2 were also pointed out. Dissolution of the amine-functionalised NTs can be achieved using the amines with long alkyl radicals since the interaction with aniline was found to have almost no effect on the solubility of the NTs.

Soluble NTs were also obtained by treating with poly(phenylacetylene).[112] Short NTs helically wrapped by the polymer molecules (the NT content in the composite was 1.9 mass % to 6.0 mass %) were dissolved in THF, toluene, chloroform and 1,4-dioxane.

The addition of poly(*m*-phenylene vinylene-*co*-2,5-dioctyloxy-*p*-phenylene vinylene) to powdered NTs allows their dissolution in standard organic solvents (*e.g.*, toluene) and purification from insoluble particles of turbostratic graphite.[113, 114] The polymer is prone to form helices with a diameter of $\sim$20 nm and a pitch of $\sim$6 nm. The NTs under study were 15 to 20 nm in diameter and 0.5 to 1.5 μm long. Because of the correspondence between the NT diameter and the diameter of the polymer helix, the polymer molecules can wrap the NTs, though in some instances they were found inside the NTs. Noteworthy is that the interaction of bright yellow polymer with black NTs resulted in a dark green composite. The nanotube/polymer suspensions were stable for a period of at least 6 months.

c. Colloidal solutions and dispersions of carbon nanotubes

Solubilisation of NTs can also be achieved by colloid chemistry tools. Functionalised soluble NTs differ from surfactant-coated NTs in strength of the bonds they form (only in the former case these bonds are covalent). Suspensions of NTs are stabilised using common surfactants.[91] Surfactant-stabilised dispersions of MWNTs and SWNTs are convenient for chromatographic purification.[115–117]

The most often used surfactants are DMF and *N*-methylpyrrolidone. Dispersions of NTs in DMF are stable.[103, 118] However, the authors of a more recent study[119] showed that these dispersions tend to aggregate after a period of several days. One can assume that NTs tested by different authors exhibited different properties.

The most stable are dispersions of NTs in strong Lewis bases which do not form hydrogen bonds.[119] These are (in the descending order of the optical density of NT dispersions) *N*-methylpyrrolidone, DMF, hexamethylphosphoric triamide, cyclopentanone, tetramethylenesulfoxide and ε-caprolactam. The optical spectra of NT dispersions in these solvents follow the same pattern. Dispersions of NTs in DMSO, acrylonitrile, 4-chloroanisole and ethylisothiocyanate follow another spectral pattern, while NT dispersions in 1,2-dichlorobenzene, 1,2-dimethylbenzene, bromobenzene, iodobenzene and toluene follow yet another, third, spectral pattern.

The third group of solvents is thought to be the best for C_{60} and C_{70} (see Ref. 120).

Complexation with polyacrylic acid and surfactants allows solubilisation of MWNTs up to several micrometres long.[121]

Exact reproduction of the geometry of NT-derived nanoscale devices required studies on the behaviour of micellar dispersions of NTs on patterned surfaces[122] and preparation of the Langmuir–Blodgett films based on amphiphilic molecules and NTs.[123] Such films were fabricated by dispersion of NTs in aqueous solution of lithium dodecyl sulfate, isolation of the residue by centrifugation and introduction of the residue into the subphase of the aqueous solution of poly(allylamine hydrochloride).

Burghard *et al.*[124] coated electrodes with NTs using surfactant-stabilised NT suspensions or Langmuir–Blodgett films. At low temperatures, SWNT bundles in the Langmuir–Blodgett films exhibit nonlinear current-*vs*.-voltage characteristics.[125]

IV. Decoration of carbon nanotubes and their use as templates

Coating of the side walls of NTs can be achieved *via* their pre-treatment (functionalisation) or without it. The first route implies the chemical interaction as a necessary stage and is often called nanotube decoration. The second route implies that NTs are used only as templates for the deposition of other substances, though in this case the chemical interaction between the NTs and the substance to be deposited cannot often be ruled out.

A clear correlation was established between the amount of adsorbed Pd^{2+} ions and the concentration of acid groups on the surfaces of both closed and open NTs and graphite.[84] Adsorption of Cu^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Pr^{3+} and UO_2^{2+} ions on the surface of functionalised open NTs was also studied. The adsorption capacity was found to range between 0.005 (UO_2^{2+}) and 0.029 (Pd^{2+}) mmol per gramme of carbon. To obtain metallic palladium using NTs, they were first reduced with H_2 at 250 °C.

Coating of acid-treated NTs with platinum clusters has been described.[85]

To show that NTs can be used as a template, they were oxidised in two steps,[124] namely, by long-term (3 h) reflux in HNO_3 followed by short-term treatment with a strongly acidic $KMnO_4$ solution (the oxidant was decomposed after less than 1 min by adding acetic acid). The oxidised NTs acquired the ability to be readily dispersed in water and to attach copolymers with hydrophobic (butyl methacrylate) and hydrophilic (4-vinylpyridine) groups. The external surfaces of the functionalised NTs were then decorated with gold nanoparticles that form a conducting layer.

Copper nanoparticles with narrow particle size distribution can hardly be obtained by conventional techniques; because of this, they were synthesised using NTs as a template.[126] The NTs used in this study were prepared by catalytic pyrolysis of CH_4. Changing the catalyst composition enabled production of NTs with different diameters and narrow diameter distributions (from 5–10 to 25–35 nm). In addition to variation of (i) the copper salt concentration in the aqueous solution and (ii) the initial ratio Cu : NTs, the procedure involved the reduction in H_2 and washing from the template by sonication and resulted in either Cu nanoparticles or nanofibres. The smaller the NT diameter and the lower the salt concentration in the solution, the smaller the diameter of the copper particles (with the smallest particle size between 5 and 10 nm). An increase in the salt concentration in the solution and the Cu : NTs ratio resulted in the formation of copper nanofibres from 100 nm to 5 μm in diameter and up to hundreds of micrometres long.

Decoration of activated NTs with copper and nickel particles in the presence of Pd complexes using one-step and two-step activation-sensitisation has been reported.[127] Both methods imply coverage of the NT surface with Pd or Pd–Sn nuclei followed by the formation of a continuous coating of the NTs with copper and nickel. The coating density was determined by the activation conditions.

The structure of the coating formed on the external surfaces of NTs interacting with molten V_2O_5 was studied and discussed by Ajayan *et al.*[51,62] This coating can be formed due to surface tension and be very thin. Vanadium oxide has a pseudolayered structure with pyramidal VO_5 units held together by bridging oxygen atoms. These layers can uniformly cover the entire surface of NTs and form thin films. Oxidation of such films in air at 650–675 °C resulted in removal of carbon and preparation of V_2O_5 flakes less than 1 nm thick and rod-like V_2O_5.

A topotactic correspondence between the oxide layer and NTs should be pointed out, *viz.*, the *c* axis of the oxide is perpendicular to the NTs axis. Mention was also made of preferred orientation of the crystallites found inside and outside the NTs (see, *e.g.*, Ref. 52).

The possibility of coordinating $Cr(CO)_6$ to NTs has been reported.[128] Molecular dynamics simulations showed that the chromium center of the $Cr(CO)_3$ group is coordinated to the three double bonds of a benzene ring of the NT side wall.

Nickel and cobalt with small additives of P and B can be chemically deposited onto the MWNT 'forest' to form a continuous polycrystalline coating.[129,130] Similar experiments on the deposition of Ni on the NTs that were dispersed in $SnCl_2$ and $PdCl_2$ solutions by sonication and transferred then into the bulk solution were also carried by Li *et al.*[131] who, however, failed to obtain continuous coating. Strong effect of the pH value of the bulk solution on the character of the coating and, in particular, on the degree of aggregation of the nickel particles was pointed out.

Decoration of NTs with complex molecules including DNA is also possible. For instance, long-term storage of the solutions of such compounds with the NTs pre-treated to be covered with acidic centres resulted in immobilisation of 'small proteins' metallothioneine, cytochrome C_3 and β-lactamase I. The fact that most parts of the immobilised proteins remain catalytically active indicates the absence of pronounced conformational changes. The adhesion force between the proteins and the surface is rather strong and the proteins cannot be washed off with water.[132]

Multi-walled NTs coated with a rhodium phosphine complex were prepared.[133]

The use of gel techniques and, in particular, sol-gel process opens considerable opportunities for NT decoration. For instance, coating of NTs with zirconium propoxide followed by calcination and burning out of carbon resulted in zirconia nanotubes.[134] After functionalisation and interaction with $Zr(OPr^n)_4$ the NTs was washed with methanol and dried at 373 K. The gel was then calcinated at 723 K and carbon was burnt out in air at 973 K. The zirconia nanotubes thus obtained were 40 nm in diameter, had the side walls 6 nm thick and represented a mixture of equal amounts of monoclinic and tetragonal zirconia phases.

Fabrication of Y_2O_3-stabilised zirconia NTs *via* gelation of colloidal solutions of $ZrOCl_2$ and $Y(NO_3)_3$ by addition of NH_4OH followed by heat treatment is a considerable step forward. A similar procedure was used for the synthesis of hollow NTs or nanorods from SiO_2, Al_2O_3, V_2O_5, Sb_2O_5, MoO_2, MoO_3, WO_3 and RuO_2.[135,136] Gels were prepared using (i) the vanadium, molybdenum or tungsten acids synthesised from corresponding salts by ion exchange technique and (ii) metal chlorides. TiO_2-Coated NTs were also prepared (this report can be accessed *via* the Internet at URL http://www.fys.kuleuven.ao.be/vsm/spm/Ti_oxidation_fig11.html).

It was established that physically deposited Ti, Ni and Pd coatings cover the surfaces of NTs by continuous or quasi-continuous layers, whereas Al, Au and Fe coatings only form isolated discrete particles on the NTs.[137,138]

Calculations[139] of the adsorption of potassium atoms on the external and internal NT surfaces showed that the process is energetically favourable for small-diameter NTs.

A theoretical study of the interaction of Ni and Ni_2 with graphite and NT side walls[140] revealed considerable differences in bonding sites, magnetic moments and the direction of charge transfer. The effect of the NT surface curvature[§] on the reactivity of graphene sheets has been studied.[141] Some conclusions drawn based on the results of quantum-chemical calculations were confirmed experimentally.

V. Substitution of the carbon atoms of nanotubes by atoms of other elements

The interest in carbon NTs in which some of the carbon atoms are partially or completely replaced by atoms of other elements, as well as the interest in the NTs made of other substances stems from the fact that these NTs can exhibit improved electronic properties as compared to the carbon NTs. For instance, the electronic

§ The study[141] concerns bending of NTs and has a new term in the title, 'Kinky Chemistry'.

characteristics of boron nitride NTs (hereafter, BN-NTs) are known to be independent of their structure.[142] Young's modulus of BN-NTs is ~1.2 TPa, which is a record value for fibrous dielectrics.[143] Therefore, BN-NTs are thought to be the best material for encapsulation of conductors in their inner cavities. This type of NTs is promising for fabrication of low-voltage field emission devices and preparation of composites from coaxial sandwiches of carbon NTs and BN-NTs.[144]

The structure and electronic properties of nitrogen-containing NTs have been studied at different N : C ratios and different structure of isomers.[145] It was found that, depending on the mutual arrangement of nitrogen and carbon atoms, NTs can exhibit either metallic or semiconducting properties with a narrow energy gap.

However, BN-NTs as well as B_xC-NTs or B_xCN_y-NTs are difficult to prepare using the procedures developed for production of carbon NTs. An original method of attacking the problem of preparation of B_xC-NTs involves replacement of the C atoms in carbon NTs by B atoms.[146, 147] Indeed, the oxidation of NTs by B_2O_3 vapours in Ar stream at 1373 K resulted in B_xC-MWNTs ($x \leqslant 0.1$) with the same diameter and length as those of the untreated NTs.

$$x\,B_2O_3 + (2 + 3x)\,C_{(NTs)} \longrightarrow 2\,B_xC_{(NTs)} + 3x\,CO.$$

It was suggested that the low degree of substitution is related to the multi-walled nature of the starting material (the untreated NTs) and that mostly the outer shells were involved in the reaction. In addition to B_xC-NTs, crystalline rod-like nanomaterials of stoichiometry B_4C and $B_{13}C_2$ were found among the reaction products.

Preparation of $(BN)_xC$-NTs from carbon NTs with an average diameter of 10 nm and B_2O_3 powder in N_2 stream at 1573 K has been reported.[148] In this case, the graphite crucible used for the synthesis of B_xC-NTs should be replaced by a BN crucible. Noteworthy, C → B substitution was found to lead to a more ordered NT structure.

The same procedure was also used for the synthesis of BN-SWNTs and carbon NTs doped with boron and nitrogen.[149]

The reaction

$$B_2O_3 + 3\,C_{(NTs)} + N_2 \longrightarrow 2\,BN_{(NTs)} + 3\,CO$$

was conducted in an induction furnace at temperatures between 1523 and 1803 K and resulted in B_xC-NTs, $B_xC_{1-x-y}N$-NTs and BN-NTs. The yield of the BN-NTs increased as the temperature increased. However, not all NTs were involved in the reaction. It is interesting that some of the BN-NTs were filled with octahedral BN particles, which resembles the formation of nanoscale 'pea-pod' structures of carbon NTs.

A more complicated procedure for increasing the yield of substituted NTs consists of MoO_3-promoted synthesis using B_2O_3.[150] The reaction was carried out at the mass ratio $B_2O_3 : MoO_3 : NTs = 5 : 2 : 1$ at 1773 K. The reaction was nearly complete after 30 min due to the stronger oxidative effect of the MoO_3 additive compared to that of B_2O_3 and resulted in the formation of BN-NT bundles up to 1 μm long. The authors of this study [150] suggest that the process begins with the oxidation of NTs following the reaction

$$MoO_3 + 3C_{(NTs)} \longrightarrow Mo + 3\,CO.$$

As a result, the NTs are opened, thus enhancing their reactivity towards B_2O_3 and N_2. The Mo atoms chemisorbed at the NT ends act as catalysts to preclude the formation of 'caps'. This is accompanied by filling the NTs with Mo-containing clusters.

Boron- and nitrogen-doped SWNTs containing up to 10 at.% B and up to 2 at.% N were produced in high yield using substitution reactions.[151] The highest yield was achieved at 1553 K after 30 min synthesis. All the SWNTs synthesised were found to form bundles with an inter-tube spacing of ~0.3 nm.

A multistage substitution reaction was used for the template synthesis of GeO_2 nanorods (NR).[152] A mixture of powdered Ge, Si and SiO_2 with carbon MWNTs 15 nm in diameter was heated in Ar atmosphere at 850 °C for 3–4 h. The overall process is assumed to involve a number of reactions of Ge vapours, *viz.*, partial exchange with SiO_2, a reaction with the carbon atoms on the NT surfaces and oxidation into GeO_2 in the presence of O_2.

$$Ge_{(gas)} + 2\,O_2 + 2\,C_{(NTs)} \longrightarrow GeO_{2(NR)} + 2\,CO.$$

Nanotubes were used for the template synthesis of SiC,[153, 154] TiC, NbC, Fe_3C and BC_x (see Ref. 153); GaN,[155] Si_3N_4 (see Ref. 156) and TaC [157] *via* reactions with volatile oxides (SiO, Ga_2O, B_2O_3), chlorides ($FeCl_3$) and iodides (TiI_x, NbI_x).

Nanotubes can be coated with titanium.[137, 138, 158]

Reactions of the type

$$xC_{(solid)} + M_{(solid,gas)} \longrightarrow MC_{x(solid)}$$

do not belong to but are much the same as substitution reactions. The interaction of SWNTs and SWNT bundles with silicon begins at temperatures above 800 °C and is accompanied by the formation of β-SiC nanorods that retain the morphology of the carbon NT bundles (this holds even for long rods!).[159] The reactions of individual NTs or NT bundles at 970 °C in ultrahigh vacuum resulted in structures with the $Si-SiC_{(NR)}-C_{(NTs)}$ heterojunctions. Similar structures with well-defined carbide–metal interfaces were obtained in reactions of NTs with titanium. A schematic illustration of the method is shown in Fig. 7.

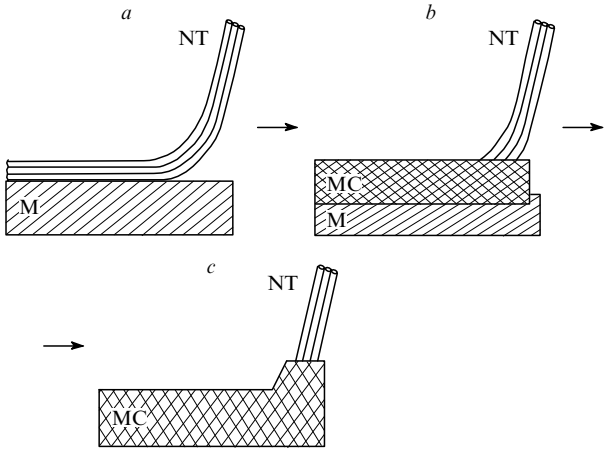


Figure 7. A schematical illustration of the method for fabricating $MC-C_{(NTs)}$ heterojunctions.
Before reaction (*a*), formation of carbide in the reaction of the nanotube with the metal (*b*) and after reaction (*c*).

Preparation of structures with $NbC-C_{(NT)}$ heterojunctions appeared to be a more difficult task due to peeling of NTs from the carbide on cooling. However, the reaction with niobium is convenient for cutting long NTs and making a uniform morphology of NT ends, which is of great importance for fabrication of field emitting devices.[160] To this end, a perforated Nb wafer was coated with a suspension of NTs, the solvent was removed and the NT-coated wafer was kept in $\sim 10^{-8}$ mm Hg vacuum at 950 °C.

VI. Insertion of 'guest' atoms and molecules into the intertubular space of multi-walled nanotubes and nanotube bundles

Intercalation compounds of carbon materials are of considerable interest in many respects. Lithium-intercalated graphite and related substances are commercially used in lithium batteries; the theoretical limit for the specific energy capacity of these materials equals 372 mA h g^{-1} and corresponds to the composition LiC_6 (see Ref. 161). Sometimes, the second electrode in lithium chem-

ical current sources is fabricated from fluorinated graphite (see, *e.g.*, Ref. 162). Fullerenes and NTs can also be used for these purposes.[163] Theoretically, NTs must possess a higher degree of intercalation than fullerenes.

Intercalation of MWNTs and SWNTs are two basically different processes. In the case of MWNTs, the intercalated particles penetrate into the space between the nested shells through topological defects and stay there.[164, 165] Single-walled NTs cannot be intercalated in this manner, but the 'guest' atoms or molecules can penetrate into the intertubular space of the SWNT bundles.

Intercalated NTs are also fundamentally different from fullerene intercalation compounds. For instance, fullerene C_{60} can form charge-transfer complexes only with electron donors.[166, 167] On the other hand, the results obtained by Raman [168] and optical [169] spectroscopy and from conductivity measurements [170] show that SWNT bundles exhibit the double behaviour typical of graphite and can be doped with either electron donors or acceptors. Charge transfer in SWNTs was also observed in many other experimental studies. This is characteristic of both metallic and semiconducting SWNTs.[169] Charge transfer in MWNTs also does occur.

The conductivity temperature coefficient of crystalline bundles of single-walled (10,10)-NTs is positive, thus indicating their metallic properties. Intercalation with Br_2 or K reduces the electrical resistance of the NTs at 300 K by a factor of 30 and extends the temperature range in which the conductivity temperature coefficient is positive. This points to the fact that Br_2- or K-doped NTs ($C_{52}Br_2$ and $C_{116}Br_2$) belong to the synthetic metals.[170]

Intercalates are ionic compounds and intercalation leads to an increase in the charge carrier density. Optical spectrometry studies [171] proved the possibility of controlled shift of the Fermi level of individual SWNTs by doping them with various substances. The results of electrochemical measurements also point to reversible doping of SWNTs ('nanopaper') with Li^+ ions in organic radical anions (naphthalene, benzophenone, fluorenone, anthraquinone and benzoquinone) and to shift of the Fermi level.[20] No intercalation stages typical of graphite intercalation reactions were observed. It was found that the chemical composition of the doped NT samples can be varied smoothly.

Absorption spectra of intercalated SWNTs in the visible region exhibit complex patterns which depend on the dopant concentration.[172]

Conclusions drawn by Iijima *et al.*[173] contradict the known idea that NT intercalation is accompanied by a rather high degree of charge transfer. The results obtained in this study should be more thoroughly analysed because of the high scientific authority of the authors.

1. Intercalation of electron donors

Multi-walled NTs [164, 165] and SWNT bundles [170, 174] are characterised by a different structure of the van der Waals spacings between individual NTs. However, both types of NTs can be intercalated with alkali metal vapours up to the composition MC_8 (M = K, Rb, Cs). The capacity of these materials is comparable to that of graphite which also forms compositions of stoichiometry MC_8 upon intercalation.

Multi-walled NT bundles increase their mass by 33% upon intercalation with potassium and by 260% upon intercalation with $FeCl_3$. The intercalation is accompanied by changes in the NT shape, volume and morphology and by swelling and formation of necks. Intercalation products can be readily hydrolysed; however, subsequent washing leads to recovery of their initial state. Different types of MWNTs (*i.e.*, with the 'Russian doll' and 'roll' structure) are believed to exhibit different intercalation behaviours.[175, 176]

In vacuo intercalation of SWNT bundles with Cs and K vapours at room temperature is reversible and leads to structural disordering of NT bundles.[177] The chemical composition of the intercalation products corresponds to the empirical formulae KC_{24} and CsC_x ($x = 8-24$). Disordered structure of SWNT bundles prevents locating the metal sites.[177] Disordering is due to presence of the metal atoms in the intertubular space rather than filling of individual NTs (the samples used in the experiments were 'capped').

Electrochemical intercalation of SWNTs with alkali metals involves three stages characterised by different rates. These are charge transfer through the macroscopic electrolyte–electrode interface, diffusion through the mesopores of the electrode and diffusion in the NT bundles.[178]

A number of studies [168, 170, 179] were carried out using 'mat'-like SWNT structures. However, NT 'mats' consist of a mixture of metallic and semiconducting NTs and the results obtained appeared to be hardly interpretable.

Chemically doped semiconducting NT bundles change their hole-type conductivity to electron conductivity.[180] A correlation between the concentration of the intercalated potassium and the charge carrier density was found. Typically, the electron density varies between 100 and 1000 μm^{-1}. The effective mobility of electrons was found to be 20 to 60 $cm^2\ V^{-1}\ s^{-1}$, which is in agreement with the corresponding numerical estimate obtained for holes.[181]

Intercalation of SWNTs and SWNT bundles with potassium also changes their transport properties.[182–184] Pichler *et al.*[184] found that at 425 K the C : K ratio in potassium-intercalated NT bundles approaches 7, which corresponds to the formation of a stage-1 intercalation compound, KC_8. According to Pichler *et al.*,[184] intercalation leads to a relatively small increase in the intertubular spacing and the total conductivity of the intercalated bundles is somewhat lower than that of the untreated NT bundles.

Molecular dynamics simulation [185] predicted the most stable structures of K-doped single-walled (10,10)-NTs. These were found to be KC_{16} (filling of the intertubular space) and KC_{10} (filling of both the inner NT cavities and intertubular space). The optimum structure corresponds to the compositions $K_5^{exo}C_{80}$ for the former type of NT filling and $K_5^{exo}K_3^{endo}C_{80}$ for the latter.

2. Intercalation of electron acceptors

As mentioned above, charge transfer occurs between the NTs and intercalated Br_2. Photoelectron spectra [42] point to the formation of surface complexes $C-Br_2$. The nature of the interaction between Br_2 and the NTs was studied by high-resolution transmission electron microscopy.[186] A preferential orientation of the bromine atoms was found, which is consistent with the results obtained in other studies. It appeared quite surprising that the region of Br_2 accumulation in MWNTs extends perpendicular to the NTs axis, which means that the liquid Br_2 behaves to some extent like a solid. The complexes formed were found to be not too stable and Br_2 can be washed off with CCl_4. Br_2-Intercalated NTs retain tubular structure, though the arrangement of the nested carbon shells becomes somewhat disordered (the NTs are 'amorphised'). After removal of Br_2, the NTs were more readily oxidised with oxygen than the unintercalated NTs.¶

The interaction of molten iodine with NT bundles in a sealed ampoule at 140 °C results in disordering within the NT bundles.[187] The two-dimensional crystal lattice of the NT bundles expands (the cross-section area increases).

In the intertubular space the iodine atoms are grouped and form $(I_5)^-$ chains separated by ~2.1 nm at moderate intercalation degrees. Intercalation reduces the electrical resistance and thermal electromotive force (emf) of the NTs. The iodine-doped

¶ A somewhat arbitrary use of the term 'intercalation' for the description of the above-mentioned processes should be pointed out. Strictly speaking, no increase in the interlayer spacing occurs in this case and the crystal lattice parameter increases insignificantly. Liquid Br_2 is adsorbed on the outer surfaces of NTs and is soaked into the inner cavity after opening the NTs due to wetting.

NTs are stable in air. More recently,[188] the poly(iodide) chains formed inside SWNTs were found to have a helical shape.

Bower *et al.*[189] studied the interaction of 70% HNO_3 with SWNT bundles and found that (i) intercalation occurs reversibly and (ii) the intertubular spacing increases upon the insertion of the acid molecules. The starting material was a 'mat'-like substance, or 'nanopaper', with the NT content of about 70%. The intercalation occurred at room temperature and, in contrast to the interaction with graphite, took a rather short time due to the capillary effect of the NT bundles and was accompanied by an increase in the intertubular spacing within the bundles. The crystallinity of the NT bundles remained after intercalation; however, an increase in the lattice parameter from $\sim$1.7 to 2.0 nm was observed. No proton abstraction from the HNO_3 molecule was suggested. The structure of the HNO_3/SWNTs intercalate is shown in Fig. 8. *In vacuo* heating of the samples to 500 K caused the onset of the reverse process. Extention of intercalation time to 12 h and longer times resulted in the loss of order within the NT bundles and in partial or complete breakdown of the NT bundles into individual NTs upon removal of HNO_3.

A study of electrochemical oxidation of SWNT bundles by H_2SO_4 revealed some remarkable features.[190] A spontaneous charge-transfer reaction was observed in the NT bundles. In contrast to the graphite–H_2SO_4 system, this reaction proceeds even before applying the potential difference. On the other hand, both systems share some common features. Under the action of electric current the NT bundles behave similarly to graphite, namely, the reaction

$$H_2SO_4 + \bar{e} \longrightarrow HSO_4^- + \frac{1}{2}H_2$$

proceeds by the 'charge exchange' mechanism and there is an 'overoxidation' regime (irreversible formation of covalent bonds C–O).

$FeCl_3$-Intercalated MWNT bundles exhibit metallic conductivity.[175, 176, 191] The temperature dependence of this parameter was studied by Baxendale and Amaratunga.[192]

Intercalation of NTs with $CuCl_2$ followed by reduction of the chloride to metallic Cu can be used for purification of the NTs.[41]

An interesting reaction was studied by Hsu *et al.*[193] The main goal of the study[193] was to obtain diamond from NTs *via* treatment of potassium-intercalated NTs with CCl_4 to give KCl and excess carbon. This reaction seems to be of no interest for large-scale implementation; however, it opens new prospects for synthetic chemistry. The authors hoped that the reaction

$$4K + CCl_4 \longrightarrow 4KCl + C$$

would result in cross-linking of adjacent graphite basal planes and in replacement of the sp^2-bonds by sp^3-bonds within the intertubular space of the MWNTs. The reaction was carried out in an autoclave at 200 °C; however, no diamond was produced. Analysis of the reaction products revealed the loss of ordering ('amorphisation') of the tubular structure and the formation of KCl crystallites within the space between graphite shells with presumably distorted structure. No KCl crystallites were found (i) within the NTs with the outer diameter of less than 10 nm and (ii) far from the outer surface of the MWNTs.

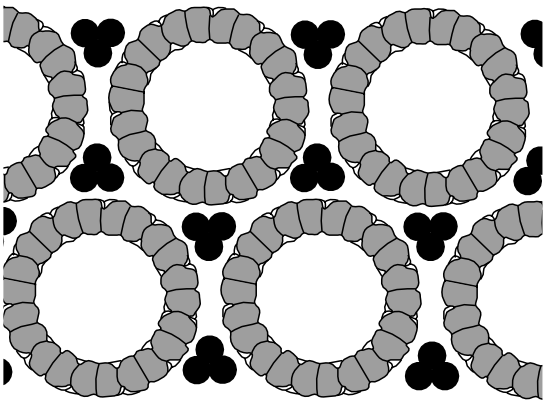


Figure 8. A model of the structure of the HNO_3/SWNTs intercalate. The C–O distance was assumed to be the same as in the case of HNO_3 intercalated graphite, the distance between the centres of the nanotube cross-sections was set to $\sim$2.0 nm.

VII. Adsorption and storage of gases in carbon nanotubes

Nanotubes can adsorb gases at high pressures or under conditions of electrochemical saturation. Adsorption can occur on the internal surfaces of NTs (within the innner cavities), on the external surfaces of free-standing NTs and in the intertubular space of NT bundles.

Pioneering calculations of the adsorption of gases on NTs were carried out by Maddox *et al.*[194]

Model calculations of the sorption of hydrogen, oxygen and chlorine atoms by SWNTs and graphite revealed three types of surface sites and provided an explanation for high efficiency of hydrogen storage in NTs.[195]

Compared to fluorine atoms, attachment of hydrogen atoms to the side walls of NTs is less probable; the attachment of two or four hydrogen atoms to a (10,0)-NT is an endothermic process.[108]

Adsorption of a Lennard-Jones gas mixture on single-walled arm-chair NTs with inner diameters of 6.125, 7.482 and 8.16 Å was theoretically studied by Ayappa.[196, 197] He showed that at $T \geqslant 388.9$ K adsorption of large particles occurs for the most part. These particles interact relatively strongly with the NTs walls. As the temperature decreases, the equilibrium is shifted towards smaller particles which completely replace the large particles at $T \leqslant 303$ K. Condensation of the small particles occurs in pores.

A series of theoretical studies on the adsorption of gases in NTs was carried out by Stan *et al.*[198–204] In the case of adsorption of inert gases on NTs the bonding between the adsorbate and the surface is stronger than in the case of graphite.[198] At low surface coverages, the adsorption strongly depends on the NT structure and size. A salient feature of the process is its one-dimensional character.

Helium and neon readily fill the intertubular space of NT bundles. They are strongly bound to the NT side walls even under those conditions where almost no adsorption occurs on the basal planes of graphite.[200] The condensed phase is strongly anisotropic. Since adsorption leads to the formation of a quasi-one-dimensional system, the properties of this system differ from those of standard systems.[201]

According to calculations, adsorption of small atoms occurs both inside NTs and in the intertubular space of NT bundles, whereas the adsorption of relatively large atoms and molecules with rare exceptions occurs only inside the NTs.[203] Helium atoms are strongly bound to the side walls within the intertubular space of NT bundles. The system can behave like a lattice gas or condensed phase; despite the fact that the content of the adsorbate atoms is at most 2% they contribute much more to the specific heat capacity than the 'host' molecules at low temperatures.[202] In the case of adsorption of a $^3He-^4He$ mixture the partial pressure of each component is determined by the ratio of their concentrations within NT bundles; the situation looks like adsorption is controlled by some rule similar to Raoult's law.[204]

A study on the desorption of ^4He at 14–23 K showed[205, 206] that the process can be described by the equation for one-dimensional adsorption of neutral particles with very high binding energy estimated as 330 K (at 14–16 K), which is very close to the calculated value (340 K).[200] Channels in the intertubular space of NT bundles can be represented by cylinders 0.21 nm in

diameter and their cross-sections can be filled by at most one helium atom. At temperatures above 16 K, the experimental adsorption capacity was higher than the theoretical value for unknown reasons.

The binding energies of other noble gases (neon and xenon) and CH_4 to the external surfaces of closed SWNT bundles are nearly 75% higher than to the flat graphite surface.[207, 208] However, neither of the gases can be adsorbed in the intertubular space of the NT bundles.

Enhanced adsorption of xenon inside SWNTs at 95 K in the presence of defects, especially after removal of carboxylic groups from the NT surface was observed.[87] The experimentally determined activation energy of xenon desorption (26.8 kJ mol^{-1}) was found to be close to the calculated value (22.6 kJ mol^{-1}).[198]

Experimental study of N_2 adsorption on MWNTs that were open at one end, with mesopores of width 4.0 ± 0.8 nm, at 77 K showed [209] that nitrogen molecules are adsorbed on both the external and inner NT surfaces. It was found that adsorption on the external surface is five times greater than that on the inner surface and that the corresponding adsorption isotherms are considerably different. Adsorption in mesopores was described in terms of the classical theory of capillary condensation and the calculated pore diameter was found to be 4.5 nm. The adsorption isotherms exhibited no hysteresis, in stark contrast to the curves reported by Kyotani *et al.*[210] who studied adsorption in mesoporous NTs open at both ends. These differences were rationalised by accessibility of only one NT end.

Single-walled NT bundles also readily adsorb N_2. Unpurified NTs prepared by the arc method were characterised by an inner specific surface of 233 $m^2\ g^{-1}$ and an external specific surface of 143 $m^2\ g^{-1}$ (see Ref. 211). Acid treatment of the NTs resulted in an increase in the total specific surface from 376 $m^2\ g^{-1}$ to 483 (HCl) and 429 $m^2\ g^{-1}$ (HNO_3) and enhanced the adsorption capacity towards benzene and methanol.

Adsorption of gases affects the electronic [212] and emission [213] properties of NTs. The effect of O_2 adsorption on the electronic and magnetic properties of NTs has been studied.[214]

VIII. Potential fields of application of carbon nanotubes

Increasing interest in NTs is due to great potentialities of their efficient use in industry.[2, 18, 215–219] Small size and unique structure of NTs determine their unusual mechanical and electronic properties (these can be controllably varied over a wide range). In contrast to graphite, NTs are free from dangling bonds and are therefore chemically inert. Nanotubes represent a highly rigid and, at the same time, elastic material that exhibits the ability to undergo reversible swelling (buckling up) and folding (compression, flattening).

The fields of application of NTs can be arbitrarily divided into two groups. The first group of applications utilises NTs in the form of relatively large devices or parts (many NTs 'function') such as light, strong, conducting (if necessary) and impact energy absorbing fillers for various composites, materials for chemical current sources and accumulators of gases. The second group of applications uses NTs in mini- and microcomponents and devices (individual NTs 'operate'). These are electronic components and devices including ultrasmall and ultrafast computers, cathodes for electron field emitters, indestructible nanoscale scanning microscope probes, high-frequency resonators, 'nanostraw' and nanopipettes for introduction into living cells to study their chemical nature.

1. Composites

a. Chemical composition and properties

Nanotubes can serve as ideal reinforcing fillers for composite materials with matrices of any chemical nature, *i.e.*, polymeric and inorganic (metals, ceramics). Many characteristics of NT-filled composite materials can reach record values. Of great importance is also the fact that NTs have low density. This allows one to obtain light composite materials. However, it should be kept in mind that the properties of NTs depend on their origin. For instance, the flexural rigidity of graphitised arc-grown NTs is ~ 1 TPa, which is two orders of magnitude higher than that of the NTs synthesised by chemical deposition of hydrocarbons.[220]

Development of methods for obtaining uniformly distributed and oriented fillers is a vital issue in the fabrication of filled composite materials. Nanotubes are characterised by large aspect ratios (1000 and more), which makes possible reinforcement of composite materials. At the same time, NTs are very short and therefore standard equipment for the production of polymers can be utilised. Using conventional long fibres imposes restrictions on the shape of finished products (carbon fibres are brittle). In the case of NTs these restrictions are removed since products of any shape can be produced by moulding.

Nanotubes are known to be highly rigid. They exhibit high axial strength [221] and a record value of Young's modulus, which approaches 1.25 TPa.[144] This value remains unchanged on going from SWNTs to MWNTs, since it is determined by the strength of the C–C bonds in individual shells.[222, 223] Not without reason theoretical estimates of possible mechanical properties of some composite materials were obtained assuming that the Young moduli of SWNTs (along the NTs axis) and diamond are comparable in magnitude.[224]

The tensile strength of MWNTs can be as high as 63 GPa, which is 50 to 60 times greater than that of high-quality steels (this material can be accessed *via* the Internet at URL http://wupa.wustl.edu/record/archive/2000/02-03-00/articles/nanotube.html).

The limiting pressure for NTs approaches 100 GPa. This is two orders of magnitude higher than for other fibres and allows the use of NTs for production of bullet-proof jackets, car and truck bumpers and for construction of earthquake-proof buildings.[225]

According to *ab initio* calculations, NTs can undergo plastic deformation.[226] Experimental studies of NTs confirmed the possibility of creating NT-derived accumulators of mechanical energy.[227] Compression of purified, oriented, highly crystalline SWNTs is accompanied by exceptionally large and reversible volume reduction. The properties of the NTs resemble those of an ideal flat spring. Under load the NT density increases smoothly to reach that of graphite, which was related to compression and flattening of entangled NT bundles. This phenomenon was also observed in studies of MWNTs.

A theoretical study on the strain and bending behaviour of NTs and the influence of defects on their transport properties was reported.[228]

The lack of the filler materials precluded extensive research into reinforcement of polymers by filling them with NTs. Nevertheless, pioneering experiments [229, 230] showed that design of various types of composite materials is possible. Single-walled NTs appeared to be the best fillers, since the inner shells of MWNTs are not involved in reinforcement.[231] Potential advantages and disadvantages of this type of composite materials have been discussed by Ajayan *et al.*[232]

Tensile test of an epoxy resin/MWNTs (5 mass %) composite showed that only the outer MWNT shells were loaded.[233] On the other hand, the results of compression test of the same composite indicated loading of all the MWNT shells.

Mechanical tests of composite materials [234–236] revealed that mechanical strength of the composites filled with MWNTs is an order of magnitude higher than that of materials filled with conventionally used fibres. The ultimate compression strength of NT-filled composite materials was found to be ~ 60 GPa, which is nearly two orders of magnitude higher than that of standard composites.[235]

The bonding between the matrix and filler in composite materials is known to be neither too weak nor too strong. In this respect the situation with NTs was unclear. The effect of the origin and concentration of SWNTs on their interaction with the

polymer matrix was studied taking PMMA-based composites filled with NTs as examples.[237] Mixtures with the NT content ranging from 1 to 20% were also studied.[238] It was found that at low NT concentrations (2.5% and 5%) the NT bundles remain unchanged, though one can assume that they do interact with the matrix since the Raman spectra indicate an increase in the intertubular spacings within the bundles.[238]

One of the nondestructive methods for increasing the surface energy of NTs consists in attachment of functional groups to the NT surfaces.[231] Chen *et al.*[102] studied solubilisation of NTs and showed that they can be dispersed in polymeric matrices without cutting. The bonding between NTs and matrix can also be increased by using defect NTs, though this can lead to some decrease in the strength of the composite material.

Of particular interest are conjugated polymer/NT composites. A salient feature of this class of polymers is the presence of an extended π-electron system that is due to the formation of a specific electronic structure with energy gaps 1.5 to 2.5 eV wide. Usually, these polymers exhibit low hopping conductivity. Introduction of NTs into composites must increase their conductivity, mechanical strength, thermal conductivity and resistance to optical damage. Indeed, a composite material with interesting optoelectronic properties was obtained from electroluminophor poly(*m*-phenylene vinylene-*co*-2,5-dioctyloxy-*p*-phenylene vinylene) and MWNTs.[113,114] The electrical conductivity of this material was measured to be eight orders of magnitude higher than that of the starting polymer. Polymer chains were found to wrap themselves around the NTs, thus making the composite material extremely strong and allowing the NTs to be suspended in the excess polymer solution. Introduction of low concentrations of NTs had little effect on the luminescent properties of the polymer. Moreover, it was found that NTs act as a nanoscale heat sink, thus preventing the composite material from overheating and destruction (under the action of, *e.g.*, laser beams).

Coleman *et al.*[239] studied the properties of poly(*m*-phenylene vinylene-*co*-2,5-dioctyloxy-*p*-phenylene vinylene)/NT composites with the NT content ranging from 0.5% to 36%. It is noteworthy that at low NT concentrations an increase in the NTs content is accompanied by insignificant increase in the conductivity of the composite material. At the NT concentrations in the range between 7% and 10% the conductivity of the material increases jumpwise by ten orders of magnitude and then again increases insignificantly at higher NT content. This behaviour is also typical of composites filled with other carbonaceous materials, *e.g.*, soot. It was found that charge transfer occurs between the polymer and NTs; however, the effective mobility of the charge carriers decreases. A study on the percolation character of the conductivity of composite materials was reported.[240] At low NT concentrations, no aggregation of MWNTs in the polymeric system occurs despite the weak interaction between the polymer and NTs.[241]

Single-walled NTs in conjugated polymers with hole-type conductivity can trap charge carriers.[242] Methods for preparation and fields of application of composite materials comprised of conjugated polymers and C_{60} or NTs were reviewed by Dai.[243]

Wrapping of polymer molecules around NTs was also observed by Seifert *et al.*[105] who polymerised phenylacetylene in the presence of NTs to prepare NTs that could be dissolved in organic solvents. The use of polymers for dissolution of NTs was studied by M in het Panhius *et al.*[244] Nanotube solutions can be used as optical filters while composite materials as converters of light into electricity.[245] Ago *et al.*[246] reported fabrication of photovoltaic devices based on NT-filled composites.

Raman spectroscopy provides the largest body of information in studies of the structure of novel carbon nanomaterials.[247] This method has also been successfully applied to composites. Raman spectroscopy allowed the researchers to follow tension due to load of an epoxy resin/NT composite material and to show that reinforcement with fibrous fillers is usually more pronounced than reinforcement with particles.[248] Wood *et al.*[249] identified the components responsible for the appearance of particular lines in the Raman spectrum of an SWNT-filled polymer, studied the effect of temperature on the spectral patterns, revealed the lines caused by thermal stress and established a stress–strain correlation.

Fragmentation of MWNTs in an urethane–diacrylate polymeric matrix under load has been studied[250] (the content of NTs was not reported).

Composites with NTs can be used for production of aligned NT arrays. By cutting thin slices (50–200 nm) of a composite material based on epoxy resin with random orientation of NTs one can obtain partial alignment of the NTs on the surface of the slice.[229] A more simple and efficient procedure involves the use of composite materials based on thermoplastic polymers. Aligned NT arrays can also be produced by mechanical tension on heated composite material followed by cooling under load.[251] The desired effect was observed only in the experiments with MWNTs.

Nanotube alignment by applying mechanical shear to a composite material sandwiched between two pieces of glass slides was reported by Tang and Xu.[112]

Composite materials based on NTs and polyvinyl alcohol[252] and polypyrrole[253] were prepared. An increase in the NT content to 10 mass % is accompanied by a sharp increase in the electrical conductivity. At higher NT concentrations, the increase in the conductivity is less pronounced.[252] Introduction of 1% MWNTs leads to an increase in the tensile strength and elasticity modulus of the polystyrene films by 36%–42% and ~25%, respectively.[254]

Nanotube fillers can be used for production of high-strength composite fibres, ribbons and coatings with enhanced wear resistance, which can find application in military, aerospace and automotive industries and pharmacy.

For instance, Andrews *et al.*[255] introduced SWNTs (Carbolex, USA) into fibres based on petroleum pitch. The filler was added to a hot pitch solution in quinoline, the solvent was removed and fibres containing 1 mass % or 5 mass % NTs (extrusion at higher NT concentrations becomes difficult) were extruded and carbonised at 1100 °C. Tests showed that the ~18-μm-diameter composite fibres with 5% NTs exhibited improved tensile strength, elasticity modulus and conductivity as compared to those of the unfilled fibres (by 90%, 150% and 340%, respectively).

An original method for fabrication of macroscopic composite fibres and ribbons incorporating flow-aligned SWNTs by forming a net from solution of NTs in a polymer followed by directed alignment was proposed.[256] Such fibres with regularly aligned NTs exhibit an elasticity modulus of 15 GPa, which is lower than that of free-standing NTs but much higher than that of, *e.g.*, 'nanopaper' (1 GPa). The fibres can be bent, crumpled and even knotted.

Reinforced PMMA fibres filled with oriented NTs were prepared.[257]

Two methods for production of composite materials based on commercially sold polymers and NTs have been developed.[258] To synthesise polymer-coated NTs, poly(ethylene glycol), poly(2-vinylpyridine), poly(4-vinylpyridine), poly(4-vinylphenol) or poly(ethylene oxide) were dissolved in DMF and NTs were added. To obtain polymer-grafted NTs, the NTs were mixed with a solution of $SOCl_2$ in C_6H_6, kept in N_2 atmosphere for 120 h, dried *in vacuo* and then triethylamine and poly(ethylene oxide) were added (140 °C, N_2, 48 h). Poly(ethylene oxide) was washed off with DMF. Thin films of the composite materials and NT solutions exhibited remarkable nonlinear optical properties.

Conducting NT-containing composite materials can be used in car body panels to replace metallic car bodies, since they allow spray painting by giving the spray electrostatic charge.[231] In this respect the properties of a composite material based on polyphenylene ether/polyamide mixture containing 10% NTs were found to be quite interesting and useful.[245] The conductivity of the epoxy resin increases by several orders of magnitude upon introduction

of minute amounts of NTs (merely 0.1 vol.%) and becomes higher than that measured after addition of the same amount of soot.[259]

It is assumed that lightweight composite materials will find use in the preparation for human Martian mission.[245]

Nanotubes can be used as additives to polymeric electroluminophors. Colouration of these luminophors occurs by giving them electrostatic charge, which makes possible painting of metallic rather than dielectric surfaces. It is believed that these limitations can be removed by introducing NTs as conductivity-enhancing additives into thermoplastic polymers.[240]

Research efforts aimed at creating chemoresistive sensors based on NT/polymer composites for a multichannel 'electronic nose' are being undertaken.

Sun and Crooks[260] reported the preparation of NT-filled polymeric membranes for sensing large neutral molecules.

Composite materials comprised of a dielectric matrix and conducting filler in the form of small extended particles can be used for electromagnetic shielding, in aerials, waveguides, *etc*. Nanotubes can serve as ideal fillers (http://www.sbirsttr.com/SbirMisc/alld991.htm). The introduction of SWNTs 10 nm in diameter (23 mass %) into ethyl methacrylate matrix leads to a nearly 35-fold increase in the dielectric constant of thick films at 500 MHz.[261]

At low NT concentrations (4% to 7%), composite materials based on NT-filled thermoplastic polymers can exhibit relatively high and uniform electrical conductivity (a short communication was posted in the Internet at URL http://www/rtpcompany.com/news/press/nanotube.htm).

Nanotubes coated with conducting polypyrrole represent a special class of materials.[262] They were prepared by polymerisation of pyrrole immediately on the NT surfaces. No chemical interaction between the polymer and NTs was observed; nevertheless, the modification led to pronounced changes in the properties of the NTs.

Methods for purification of NTs can employ stability of NT solutions in polymers[113,114,263] or the difference in precipitation rates between NTs and impurities in polymer solutions.[264,265] The proportion of short and thin NTs increases upon purification.[263]

A NT/crystalline C_{60} composite was prepared (see Ref. 266).

Research into metal/NT composites has been less intensive compared to studies on polymeric composite materials. Xu *et al*.[267] studied the morphology, mechanical and electric properties of NT/aluminium composites obtained by hot pressing of powder-like mixtures. Introduction of NTs leads to a slight increase in the electrical resistance of aluminium at room temperature and to a sharp drop of the resistance at 80 K. Related composites were prepared and investigated by researchers from Japan (this material can be accessed *via* the Internet at URL http://www.mrs.org/publications/jmr/jmra/1998/sep/013.html). It was found that hot pressing or hot extrusion do not damage NTs and that the NTs do not form products of chemical interaction with aluminium. In contrast to aluminium produced by powder metallurgy, mechanical properties of the aluminium/NT composites remained virtually unchanged upon annealing (873 K).

Introduction of NTs into a titanium matrix substantially increases its hardness.[268]

A composite NTs(3%)/metallic glass $Fe_{82}P_{18}$ was prepared by pressing a mixture of powdered starting components with NTs, melting and quenching of the melt on a copper wheel rotating at a linear speed of 30 m s^{-1}. Composite ribbons 40 μm thick were characterised by uniform distribution of the NTs that retained their initial structure.[269] Some of the NTs 'capped' at both ends were filled with iron alloy.

The number of studies on the composites with ceramic matrices is a little more than those concerning the composites with metallic matrices. Introduction of NTs into composites with $Bi_2Sr_2CaCu_2O_{8-\delta}$ (a Bi-2212 superconductor) has the same effect as irradiation of the Bi-2212 by heavy ions and favours an increase in the current density.[270] Nanotube composites with superconductors of other chemical composition were also studied.[271–273]

To prepare NT/Fe/Al_2O_3 composites, Laurent *et al*.[274–276] calcined amorphous solid solution $Al_{1.8}Fe_{0.2}O_3$ at 1025–1100 °C and then reduced it with a 88% H_2–12% CH_4 mixture at 1050°C. Calcination at 1100 °C resulted in the formation of a solid solution α-$Al_{2-2x}Fe_{2x}O_3$ ($x < 0.1$) and trace amounts of the Fe-enriched phase α-$Al_{2-2y}Fe_{2y}O_3$. Iron particles isolated upon reduction of this phase catalysed the growth of flattened (ribbon-like) arrays of NT bundles. It was found that homogenenous solid solution α-$Al_{1.8}Fe_{0.2}O_3$ with large specific surface area (this favours an increase in the NT yield and improves NT quality) can be obtained only at temperatures between 1025 and 1050 °C. This method results in two-walled NTs with an average inner diameter of ~2 nm as the main product. The proportion of SWNTs was nearly 20%.

The same authors reported the synthesis of powder-like NT/Co/MgO mixtures.[277]

b. Space cable

In 1910 F A Tsander put forward an idea of connecting the Earth and the Moon by a cable. More recently this idea was transformed into the concept of a transport cable connecting the Earth and a geostationary artificial satellite {for references, please visit the Internet Website at URL [http://www.isd.net/anowicki/SPBI120.HTM]**D**}. Conventional space rocket mass transportation systems would travel a predetermined length to transfer cargo and then mass transportation would be performed along the cable due to the action of centrifugal force.

However, no materials suitable for such a cable have been developed as yet. Polymers are vulnerable to space radiation while steel has too high density so a steel cable must have enormous weight. The best commercially available fibrous material based on specially prepared polyethylene fibres, 'Spectra 1000', has a characteristic length of 315 km. (Characteristic length is the maximum length of a cable that can carry its own weight). Recently, NASA's specialists returned to the idea of implementation of a space elevator using a NT-based fibre. The calculated characteristics of this fibre and other materials are listed in Table 1.

Table 1. Properties of particular fibrous materials (http://www.isd.net/anowicki/SPBI1MA.NTsM).

Material	Tensile strength /Pa	Young's modulus /GPa	Density /kg m^{-3}	Longitudinal speed of sound /m s^{-1}
Steel	1–5	200	7900	5000
Beryllium fibre	3.3	310	1870	12870
Boron fibre	3.5	400	2450	12778
Fused silica	–	73	2200	5760
Pyrex glass	–	62	2320	5170
E-Glass fibre	2.4	72.4	2540	5339
S-Glass fibre	4.5	85.5	2490	5860
Kevlar-49 (aramid fibre)	3.6	130	1440	9502
'Spectra 1000'	3.0	170	970	13239
PBO[a]	5.8	365	1580	15199
Carbon fibre	2–5	250–830	1850	11600–21200
Buckytube cable (theoretical data)	150	630	1300	22014

[a] PBO is poly(*p*-phenylene benzobisthiazole), a plastic fibre.

As can be seen, none of the other materials is comparable to the NT cable in tensile strength. The NT cable also must have the greatest characteristic length.

c. Artificial muscles †

As long ago as 1940s it was found that fibres made of polymeric gel-like materials compress in acidic solutions and extend in alkali solutions. The phenomenon can be used in practice by changing the direction of direct electric current. This idea provides the basis for the development of actuators and artificial muscles. For some time, conducting polymers were thought to be the most promising material for electrochemical actuators.[278] However, recent studies [279, 280] revealed that NTs are even more promising.

To function, most of the previously studied materials required application of a voltage of at least 30 V, whereas the operating voltage for 'nanopaper' varies from 1 and 4 V.[279, 280] The new material is characterised by a deformation (changes in linear dimensions) of ~1% and is capable of developing a maximum force of $\sim 3 \times 10^7$ J m^{-3} per cycle, which is about 30 times greater than the characteristics of the best ferroelectric, electrostriction and magnetostriction materials and is even greater than the force developed by human muscles. Schematic representation of the 'nanopaper' test device is shown in Fig. 9 and the relative elongation-*vs*.-voltage curve of this actuator is presented in Fig. 10.

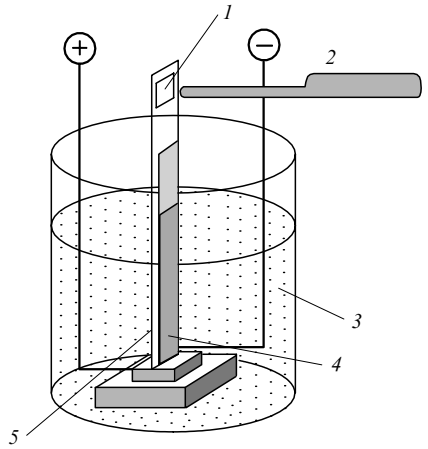


Figure 9. A scheme for a 'nanopaper' test device.
Mirror (*1*), optical sensor (*2*), electrolyte (*3*), 'nanopaper' ribbons (*4*) and insulator, a poly(vinyl chloride) film (*5*).

'Nanopaper' was studied electrochemically.[281] Samples with apparent densities of 0.30 to 0.40 g cm^{-3} containing NT bundles 1.2 to 1.4 nm in diameter were tested in various electrolytes, in the presence of both light and heavy ions, over a wide range of pH values and at different voltage scan rates. It was found that, in contrast to other forms of porous carbon, the capacity of 'nanopaper' depends only slightly on most of the parameters studied (except for the regions characterised by very low and very high pH values). Typically, the 'nanopaper' capacity varies between 18.0 and 40.7 F g^{-1} in 1.0 M NaCl solution at 0.4 V and a scan rate of 50 mV s^{-1}. These results show that pores inside the NT bundles are readily accessible to ions of different size and charge and that, at least for small samples, penetration of the electrolyte into the pores is not controlled by diffusion. The charging mechanism is described by the equation

$$\rangle C{=}O + H^+ + \bar{e} \longrightarrow \rangle COH.$$

The results obtained in these studies are of great importance for further development of not only electromechanical actuators, but also supercapacitors, sensors, *etc*.

† Information presented in this Section does not take into account the results obtained for many new chemical systems that are thought to be potentially used for the creation of artificial muscles.

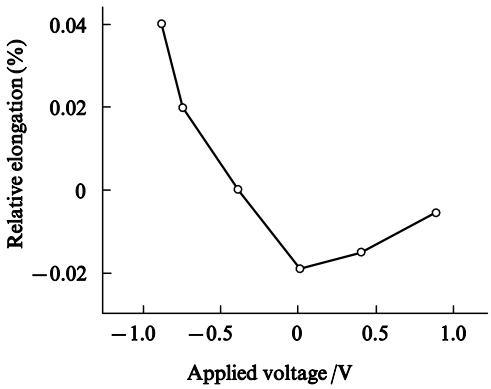


Figure 10. A relative elongation-*vs*.-voltage curve for a 'nanopaper' actuator.[279]

Che *et al*.[282] experimented with an actuator made of a 'nanostructured carbon material' (most likely, NTs).

Potential fields of application of artificial muscles cover a rather wide range from mechanical actuators that operate under severe conditions (as, *e.g*., 'windshield wipers' for space vehicles, in jet engines at 1000 °C, *etc*.) to prostheses, though the last-named task requires considerable research and development efforts and is quite time-consuming. The reverse process, *i.e*., conversion of mechanical energy into electric energy, can draw attention in the context of development of electric generators that use the energy of sea waves.

2. Fields of application of nanotubes in electronics ‡

Miniaturisation (the characteristic size of electronic chips is halved every 3 years) and improvement of performance of silicon-based electronic devices should sooner or later stop (see, *e.g*., Ref. 283). On going from micrometre (0.3 – 1.0 μm) to nanometre scale (~10 nm) electronics comes into the world of quantum effects and materials change their behaviour. Industry will make this step in the coming decade, this makes research aimed at developing new electronics vitally important.

The use of single molecules or quantum dots as functional devices can be considered the ultimate point of miniaturisation process. However, electrical contacts can hardly be attached to molecules. Therefore, the most promising candidates for practical implementation in molecular electronic devices are NTs, which can serve as the basis for creation of a new generation of integrated circuits (ICs). Search for suitable chemical substances for future electronics has been carried out since the mid-1990s. Recently, research plans were corrected and focussed on NTs.[284 – 287]

Depending on their structure, NTs possess metallic or semiconducting properties (see, *e.g*., Refs 288 and 289). For this reason alone they can be used for fabrication of heterostructures with metal – metal, metal – semiconductor and semiconductor – semiconductor junctions. In this respect particular emphasis is placed on SWNTs.

Nanotube conductivity is of quantum character.[290 – 293] Defect-free metallic NTs appeared to be ballistic conductors of electric current that flows without heat release. The current density can reach a colossal value of 10^7 A cm^{-2} and, were NTs classical conductors, they would be immediately vaporised. Ohm's law is not valid for ideal ballistic conductors, namely, their resistance is independent of length and approaches a theoretical (quantum) limit of 6500 Ω. The conductivity in NTs differs from that in two- and three-dimensional systems and can be described in the framework of the Luttinger liquid theory.[294, 295]

‡ In this Section, we present the results of selected research studies in physics and technology that are of prime interest for chemists.

Nanotube conductivity also differs from conductivity in conducting polymers where free electrons are supplied by dopants. Graphite is characterised by delocalisation of one of the four valence electrons. Graphene is an electronic hybrid; it is neither a dielectric nor a conductor, and also not a metal as well. Rather, it is a zero-gap 'semimetal' or semiconductor. Therefore, the properties of graphene depend on some extra conditions, in particular, the manner of rolling into NTs.

Of course, there is no need to discard silicon-based electronics with billion-dollars investments and start new, NTs-based electronics at the very beginning, the more so as many problems (in particular, high surface resistance of contacts, *etc*.) are still to be solved. On the other hand, production of various devices exploiting unique electronic properties of NTs that will function along with 'old' electronic is thought to be a short distance in the future. This can be a new generation of electronic and logical microchips and mechanical and electromechanical devices. Theoretically, the switching rate of NT-derived electronic devices can be as high as 10 THz. It is believed that the first step of new electronics will be fabrication of hybrid circuits. Therefore, Si-supported NTs have been the subject of intensive studies.

a. Diodes and transistors

Semiconductor diodes (two-electrode elements with one junction) and transistors (three-electrode elements with two of more junctions) are main building blocks of ICs. It is these components that first of all appeared to be the focus of research activity.

Junctions can be formed in several ways, namely, by matching two NTs (in particular, NTs of different diameters) with different electronic properties; by bending NTs; by partial filling of the inner NT cavities with those substances that give the filled parts of the NTs distinct electronic properties; by branching NTs or by making them three-terminal (Y- or T-shaped NTs). Matching two NTs with different structures requires insertion of pair defects (pentagon – heptagon) into their hexagonal atomic sheets. If the pair defects form a 'belt' along the circumference of the junction, the NTs keep their coaxial structure. If the defects are arranged opposite each other, the NTs become bent (Fig. 11). Bent NTs do exist and can be found among products of catalytic pyrolysis of hydrocarbons, as was reported by Han *et al*.[296] who observed NTs bent at angles from 18 to 34 °.

Service *et al*.[297] reported the first, theoretical, study on the subject. Insertion of pair defects into the NT structure was studied [298–302] and their energy characteristics were discussed.[303, 304]

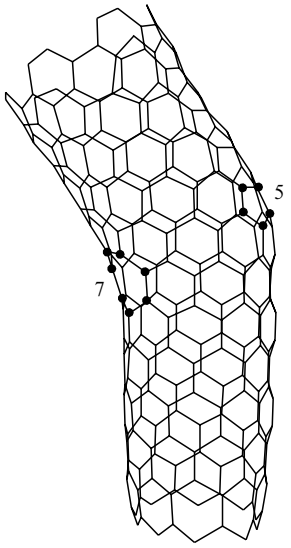


Figure 11. Schematical representation of a bent nanotube with topological defects.

Rectification of alternating electric current by a molecular diode comprised of semiconducting SWNTs and impurity molecules has been studied by Antonov and Johnson.[305] A number of theoretical studies is devoted to the properties of different junctions. [306–309] Nanotube junctions can function as Schottky barriers.

A prototype of single-electron transistor was first fabricated from SWNT bundles.[290] This type of transistor can also be assembled from free-standing NTs.[291, 310] Yao *et al*.[311] found that a bent NT with metal – semiconductor junction functions as diode rectifier. Among a total of nearly 500 NTs they found four nanotubes with one junction and one NT with two junctions and studied their current-*vs*.-voltage characteristics and the temperature dependence of conductivity.

A prototype of single-electron MWNT transistor was fabricated [312] {for references, please visit the Website at URL [http://haithabu.fy.chalmers.se/abstracts/031-html]**D**}. Researchers from Japan reported high operational characteristics of diodes based on NTs with homo- and heterojunctions.[313]

Nanotube-based field effect transistors were called TUBUFETs by analogy with the abbreviation MOSFET (Metal Oxide – Semiconductor Field-Effect Transistor).[314] Characteristics of the TUBUFET transistors fabricated from aligned SWNT arrays approach those of silicon-based MOSFET transistors. IBM Corp. (USA) also reported successful development of SWNT- and MWNT-based field effect transistors (for references, visit IBM 's Website at URL http://www.research.ibm.com/nanoscience/nanotubes.html). Researchers at IBM believe that NT-based transistors will soon be quite competitive with silicon transistors.

Junctions consisting of two crossed SWNTs (a metallic NT and a semiconducting one) were studied experimentally.[315] This type of junction can be readily fabricated and they can serve as the basis for large-scale production of useful devices.

Fabrication of integrated circuits of NTs requires enabling controlled growth and arrangement of NTs in the space between electrodes. A feature article by Dai *et al*.[316] concerns methods for the synthesis of NTs and integrated NT-based devices; particular emphasis was placed on SWNTs. The authors of this study pointed to the fact that, in contrast to traditional architectures of microelectronic devices and ICs based on the 'top – down' fabrication techniques, the methods being developed for NTs are based on the 'bottom – up' approach.

Lefebvre *et al*.[317] briefly outlined different techniques for fabrication of ICs incorporating SWNTs. Using electron beam lithography and nanomanipulation with an AFM, they showed the possibility of fabricating diodes, devices with junctions between matched individual SWNTs, single-electron transistors and field effect transistors. This study seems to be the first communication that concerns the effect of chemical environment, *i.e*., the adsorbate molecules, on the characteristics of electronic devices, since adsorption can change the electronic properties of substances when fabricating nanometre size NT-based devices. Mention was also made of the effect of mechanical deformation on the functional properties of NTs.

Very recently, strong limitations on the use of NTs in electronic devices were found.[318] They are due to specific noise that appears as electric current flows through NTs. Impurities adsorbed on the external surface of NTs are thought to be the source of the noise (or one of the noise sources). If so, NTs will enable production of very sensitive sensors.[319] Noise reduction can be achieved by simply cleaning the NT surfaces.

In a continuation of their research [318] Collins *et al*.[320] studied the effect of O_2 impurity on the electrical conductivity and thermal emf of NT bundles and films. It was found that adsorption of O_2 (i) changes the *n*-type conductivity of the NTs to *p*-type conductivity, (ii) increases the NT conductivity by 10% to 15% as compared to the value in vacuum and (iii) changes the thermal emf from -10 to $+20\,\mathrm{mV\ K^{-1}}$.

Model calculations predict that bonding of O_2 molecules to SWNTs will affect their electronic and magnetic properties.[214]

Electronic devices can be fabricated by controlled deposition of individual SWNTs with attached CO_2H groups through a mask on the surface that was chemically pre-functionalised with NH_2 groups.[118] Another closely related technique [321] involves plasma etching prior to the adsorption of functionalised NTs. Both procedures allow a space resolution of several micrometres.

Schematic representation of a chemical process of fabrication of integrated circuits incorporating nanotubes by pyrolysis of CH_4 on a Fe–Mo catalyst patterned by electron beam lithography is shown in Fig. 12.[322] Recent developments in this field allow fabrication of metal–horizontally aligned NT arrays–metal structures [323] or three-dimensional Si–vertically aligned NT arrays–metal aggregates [324] on silicon substrates using lithography and chemical vapour deposition.

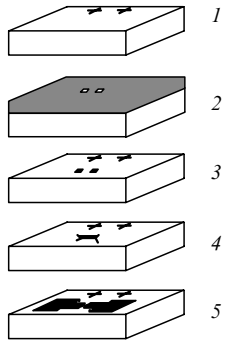


Figure 12. A scheme illustrating the order of operations in the production of integrated circuits with embedded nanotubes.[322]
Patterning with Ti–Al alloy (*1*), coating with PMMA with Petri dishes (*2*), catalyst deposition on the Petri dishes and dissolution of PMMA (*3*), chemical vapour deposition of nanotubes by catalytic pyrolysis of CH_4 (*4*) and coating with metallic electrodes (*5*).

Tests for the best ohmic contact between NTs and metallic electrodes were carried out with Ag, Al, Au, Ca, Cr, Mg, Nb, Ni and Ti.[316] The lowest contact resistance was found for titanium. One can also use Sc and V in addition to Ti, whereas Fe, Co, Ni and Cu exhibit high contact resistance.[325] A procedure for improving the stability of contacts with Ti–Al electrodes involves short-term (30 s) heating at 600–800 °C.[326] Special research into MWNT-based electrical contacts carried out to develop a fabrication procedure resulted in a rather simple method consisting in placing a tungsten wire 4.3 μm in diameter (a shadow mask) crosswise on the MWNTs, deposition of a conducting layer and removal of the wire.[327]

Since chemical methods for fabrication of NT-based devices are currently in a primitive state of development, the problem of manipulating NTs is usually solved by using scanning probe microscopes.[312, 313, 328]

Some rather exotic types of NTs have been studied. Molecular dynamics simulation revealed the possibility of fabricating metal–semiconductor–metal junctions in three-terminal NTs taking T-shaped [329] and Y-shaped [330] NTs as examples. Electronic properties of these systems were also studied theoretically.[331–333]

Branched NTs (a mixture of Y-, T- and L-shaped NTs) were first obtained in low yield by the arc method.[334] Formation of Y-shaped NTs in the course of hot wire activated CVD synthesis of diamond was reported.[335]

Higher yields of this type of NTs can be obtained by other methods, *e.g.*, CVD in the course of pyrolysis of hydrocarbons [336–338] and transition metal catalysed decomposition of C_{60}.[339] Branched NTs were also obtained by pyrolysis of acetylene followed by deposition on an Al_2O_3 template with electrochemically etched, Y-shaped channels, which was dissolved after completion of the process.[336] Microwave plasma enhanced pyrolysis of CH_4 diluted with H_2 was catalysed by nanocrystalline Pd on the surface of porous silicon.[337]

Yet another procedure for the synthesis of Y-shaped NTs involves pyrolysis of a gaseous nickelocene–thiophene mixture at 1000°C.[338] The yield of ~40 nm-diameter, Y-shaped NTs with an angle of nearly 90° between the junctions was as high as 70%. Asymmetry of the current-*vs*.-voltage curves of these NTs with respect to the bias current points to the fact that the NTs function as rectifiers. These synthetic results were found outstanding.[340]

A chlorophyll-containing protein in spinach is capable of not only receiving photons of light, but also transmitting electric signals in one direction at a rate 100 times faster than in silicon photodiodes. A nanodiode 10 nm long was fabricated from the molecules of this protein. Using 2-mercaptoethanol, the protein molecules were oriented perpendicular to the surface of a gold support and then connected by NTs to give a biomolecular device. This biochip was first demonstrated in spring 1999. Illumination by a pulse of light caused the device to conduct an electric current {this material can be accessed *via* the Internet at URL [http://www.ornl.gov/ORNLReview/rev32_3/brave.htm]**D**}.

b. Field emission devices

Cathode-ray tubes (CRT) with hot-cathode electron sources appeared more than 50 years ago. Now it is timely to replace CRT by compact flat panel displays with field (or tunnel) emitters.[341, 342] Field emission, *i.e.*, the emission of electrons from highly curved surfaces (tips, blades, *etc*.) under influence of an applied voltage, is usually observed only in ultrahigh vacuum at high voltages and the emission current is limited to several μA. Fabrication of field emitters is complicated and expensive since tips are made of single-crystalline silicon or diamond pyramids. However, these devices offer some clearly seen advantages over the hot-cathode sources, such as operation in the cold emission regime, small size, small energy expenditure in the operating mode and high density of the emission current. Because of this, field emitters have been the subject of intensive current research. For instance, it was found that ~7 μm-diameter carbon fibres used as field emitters operate under somewhat lower vacuum than other materials do (see, *e.g.*, Ref. 343).

Graphite is characterised by a relatively high work function of electrons (4.4 eV) and many graphite-based materials (in particular, micro-coarse, powder-like, ion-irradiated graphite) can be used for fabrication of field emitter cathodes. However, all of them have a great drawback consisting in rapid degradation under operating conditions. Nanotubes were proposed to be used as field emitters based on similarity of the field emission mechanisms from graphite materials and NTs.[344] Large aspect ratio, small radius of curvature of the NT end, high electrical and thermal conductivity and chemical stability of NTs make them promising for field emission applications. Not only individual NTs, but also NT bundles can serve as field emitters and function in moderate vacuum.

Schematic representation of an NT-based field emitter is shown in Fig. 13.[345]

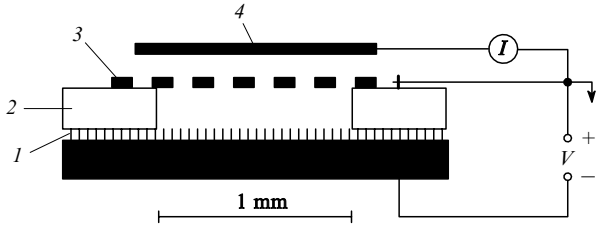


Figure 13. A scheme of a nanotube-based field emitter.
A film comprised of nanotube arrays grown perpendicular to the support surface (*1*), insulator (mica) (*2*), grid (*3*) and anode (*4*).

Let us consider the properties of NTs as field emitters. For purified MWNTs, the work function for electrons is 4.3 eV and increases up to 4.8 eV on oxidation of the NT surface.[346] The work function for NT-containing films is much lower than for graphite, though it depends on the film surface relief.[347]

Pioneering experimental studies of the emission properties of NTs were carried out by Chernozatonskii *et al.*[348] in the Russian Federation and by Ugarte *et al.*[349, 350] (in Western countries) who fabricated NT-based field emitters. An NT-based cathode can have a surface area of up to several hundreds of square centimetres, it is cheap and stable in air. However, the procedure for fabrication of aligned NT arrays (suspension, filtering and fixation of precipitate) proposed by Ugarte *et al.*[349, 350] was found to be too complicated to be used in large-scale production.

Nanotubes are characterised by emission current densities of up to 10 mA cm^{-2} at a rather low gate electric field (0.8 V μm^{-1}).[351, 352] The gate fields for SWNTs are lower than for MWNTs; however, the latter have longer lifetimes.[353]

Both open and closed NTs can emit electrons. The effect of opening of the NT ends on the emission properties has been studied.[354] Free-standing MWNTs 10 to 15 nm in diameter were produced by arc method and opened by oxidation in air at 650 °C or by laser ablation. It was found that (i) opening of NTs enhances field emission and (ii) opening by oxidation in air is more efficient than laser ablation. In their short review Schonenberger and Forro [222] pointed out that closed NTs are more efficient emitters. Theoretically, open NTs must produce higher emission currents than closed NTs; however, impurities (*e.g.*, oxygen atoms) attach themselves to the free dangling bonds at the end of the NT and the emission current reduces. Nevertheless, in both cases the emission current reaches colossal values for such small-size emitters. Emitters based on aligned arrays of 'capped' MWNT were found to exhibit the most reproducible properties and the longest lifetimes.

Nanotubes operating in the field electron emission mode emit light.[355, 356] In a dark room, the glow can be seen by the naked eye. This phenomenon is of great importance for understanding the emission mechanism.

Nanotubes produced by different methods and having different structures possess markedly different emission properties (Table 2).[357]

Table 2. Average field amplification coefficients (β), trigger and threshold electric field strengths (E_t and E_{thr} /V μm^{-1}) and average NT lifecycles (τ /h) at a current density of 0.2 mA cm^{-2} for different NT samples.

NT	β	E_t	E_{thr}	τ
Multi-walled nanotubes				
open	1100	4.5	30	20
closed	1600	1.1	2.2	120
catalytic	830	5.6	14	10
Single-walled nanotubes	3400	1.5	3.9	12.9

Kim *et al.*[359] fabricated field emitters with improved characteristics (β = 17 000 – 33 000, $E_t \leqslant 1.0$ V μm^{-1}, the brightness of the green phosphor was 1800 cd m^{-2}) using highly dense (5 – 10 μm^{-1}), well-aligned NT arrays. Diamond-'capped' silicon whiskers are characterised by record values of the turn-on (E_t) and threshold (E_{thr}) fields; however, parameters of the best samples of NT-based field emitters approach them.[358]

Characteristics of field emitters are closely related to the methods and conditions for the synthesis and purification of NTs.[44, 360] Experiments with NTs grown by plasma-assisted CVD showed that the emission current can change by an order of magnitude upon variation of the procedure for coating the catalyst (at different substrate – solution contact times).[361]

Information reported in studies on the field emission from NTs is often contradictory and the mechanism of the process is still to be clarified. The limiting field emission currents differ by orders of magnitude. Some contradictions were eliminated by Dean and Chalamala [213] who showed that saturation of the emission current is due to the presence of adsorbed impurities (the effect of saturation is observed at voltages between 1600 and 1800 V and leads to deviation of the emission currents by 2 to 4 orders of magnitude from that expected from the Fowler – Nordheim theory) . On the one hand, the presence of impurities favours an increase in the emission current. On the other hand, the impurities are removed as the emission current increases and after some time the dependence follows another pattern. Predesorption of impurities by heating samples *in vacuo* eliminates the saturation effect and reduces the emission current.

Electron energy distribution for emitting *n*-Si-supported SWNTs has been studied.[362] The observed current densities were as high as 25 mA cm^{-2}. The emitter appeared to be stable with time and exhibited well-reproducible properties. A similar study on SWNT bundles was carried out.[363]

Emission from NT bundles gives a bright structureless spot on a phosphor screen. Unexpectedly, emission from a free-standing NT with an open end gave a conical spot. The cone angles were estimated at $\sim$0.2 rad for the external and 0.05 rad for the internal parts of the cone.[364, 365]

Field emitters can also be fabricated from entangled NT arrays. The emission current density achieved in experiments with a material incorporating randomly oriented NTs (according to Collins and Zettl,[353] this favours elimination of defects) was as high as 400 mA cm^{-2} at 200 V. Cathodes for field emitters can be fabricated from NTs sintered under mild conditions (2273 K, 25 MPa).[366]

Dai and Mau [367] discussed some of the known methods for fabrication of aligned NTs. These methods can be arbitrarily divided into two groups. The first group comprises two-step procedures that involve individual stages of NT synthesis and alignment , namely, the above-mentioned cutting of thin composite slices,[229, 368] passage of a NT dispersion through a microporous filter [350] and rubbing a NT-coated plastic surface with a thin Teflon plate or Al foil.[349]

The second group comprises one-step methods that involve synthesis-induced alignment of NTs and are of much greater importance. These are template synthesis using microporous substrates and synthesis with patterned catalyst coated on the substrate surface (possible patterns are strips, squares, *etc*). Usually, experiments are carried out using Al_2O_3 membranes with parallel pores obtained by anodisation of Al, mesoporous SiO_2 and porous silicon as microporous substrates. The catalyst is either deposited on the bottom of micropores by CVD or sputtered onto the substrate surfaces that were pre-treated by lithography or programmed etching. Precipitation of catalyst from solutions is also used.

Fabrication of ordered structures from NTs by thermal decomposition of silicon carbide represents a special case.[369, 370]

Nanotube synthesis using porous Al_2O_3 has been described [129, 350, 371 – 375] (some of these studies do not concern fabrication of field emitters). The diameter, length and degree of ordering of NT arrays are completely determined by the properties of the template and can be varied over a rather wide range. Synthesis of NTs using mesoporous SiO_2 has also been reported.[376 – 378]

Fan *et al.*[379] succeeded in growing a 'forest' of NTs with uniform length distribution on the surface of porous n^+-Si substrate with an area of $\sim$4 cm^2 by catalytic pyrolysis of C_2H_4. Catalytic iron particles were deposited on the silicon surface through a shadow mask. It is thought that this method can be applied to larger surface areas (Fig. 14). The MWNT 'forest' was grown perpendicular to the substrate and presented regularly arranged, square (2 × 2 μm) NT arrays, or towers, of the same height varied in the range from 10 to 240 μm. Each of the 15 samples fabricated by the authors of this study [379] exhibited stable low-voltage electron emission. Considerable advantages of

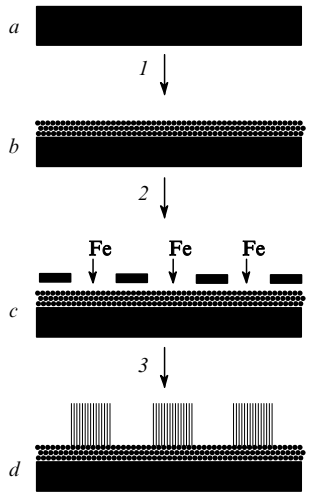


Figure 14. A scheme illustrating the process of fabrication of aligned NT layers on the surface of porous silicon.
Anodisation (*1*), sputtering of iron (*2*) and growth of NTs (*3*); n^+-silicon (*a*), porous silicon (*b*), mask (*c*) and product (*d*).

porous silicon in the synthesis of oriented NTs were pointed out. (A special issue of the journal '*Physica Status Solidi A*'[380] was dedicated to the preparation, properties and applications of porous silicon). The substrate surface can be patterned with the catalyst either lithographically or by vaporising a fraction of pre-coated catalyst.

Fabrication of field emitters from SWNTs is a more complicated problem. Nevertheless, the use of pyrolytic method and substrates patterned with 1 to 5 μm wide catalytic islands resulted in the synthesis of NTs that were 0.7 to 4.0 nm in diameter and bridged adjacent islands.[322, 381, 382] A special procedure was developed for the deposition of NTs on top of Si 'towers' pre-coated with catalyst using a contact printing technique.[383] The NT structures obtained resembled power lines with suspended SWNT bridges.

Related NT structures of some larger size were fabricated by researchers from the Russian Federation. Nanotubes for field emitters were grown by catalytic pyrolysis of acetone or by disproportionation of CO on silicon whiskers.[384]

Enhanced performance of acetylene pyrolysis and an increase in the surface area for NT deposition can be achieved by patterning the substrate with the catalyst using microcontact printing technique.[385] Experiments were carried out using hydrophilised polydimethylsiloxane as 'stamp' and solutions of iron, cobalt and nickel nitrates or their mixtures in ethanol as 'ink'. The method allows one to obtain NT strips $\sim$10 μm wide, grow NTs 5 to 15 μm high and control the NT density on the surfaces.

Fabrication of NT structures by pyrolysis of hydrocarbons in the presence of volatile catalyst or by pyrolysis of the chemical NT precursors containing both the carbon source and metal catalyst [386–390] represents a special case. [To some extent, decomposition of a $Fe(CO)_5-C_2H_2$ mixture [391] also falls in this category].

There are two ways for fabricating NT structures on thermally unstable substrates, in particular, polymeric materials. These are transfer of the precipitate obtained on thermally stable materials to polymer and reduction of the pyrolysis temperature by introducing particular additives into the chemical composition of the starting gas mixture followed by physical activation of the process. For instance, pyrolysis of C_2H_2 in excess NH_3 allowed NT deposition immediately on the low-melting glass.[392, 393]

Polymeric substrates are coated with NT 'forests' using NT deposition on quartz glass followed by dissolution of the substrate and oriented transfer of the precipitate.[321, 388]

Hot filament activated pyrolytic synthesis of NTs on different substrates was developed by researchers from France.[394] By varying the reaction conditions they grew carbon nanostructures with different morphologies and emission characteristics. It was shown that a coral-like material containing NTs and nanoparticles with reasonable emission properties can be deposited immediately on the glass surface.

Catalytic pyrolysis was used for NT deposition from gaseous hydrocarbons and fabrication of field emitters from entangled randomly oriented NTs on large surface areas.[395]

Emission characteristics of oriented NTs grown by glow discharge method from a CH_4-H_2 mixture were studied by researchers from Moscow and Novosibirsk, Russian Federation {this material can be accessed *via* the Internet at URL http://carbon.phys.msu.su/MRS/Mrs.htm]**D**}.

Emission properties of an NT 'forests' grown pyrolytically from C_2H_2 on oxidised Si surfaces coated with nickel, cobalt or a nickel–cobalt alloy were reported.[396–400]

Swiss researchers grew NTs on a silicon substrate and showed that field emission is observed without preliminary treatment of the deposited film and even in the presence of catalyst.[401] The work function for electrons was estimated to be 5.3 eV.

Field emitters are produced in the USA, Japan, Russian Federation, Australia, in EC and South-East Asia. It was shown that NT-based field emitters can exhibit improved technological characteristics (density of emission current, gate voltage, brightness and lifetime) compared to analogous devices made of other materials and hot-cathode emitters. For instance, experiments at the Oak Ridge National Laboratory (USA) showed that NT-based field emitters are 10 times more efficient than diamond ones {this material can be accessed *via* the Internet at URL [http://www.ornl.gov/ORNLReview/rev32_3/brave.htm]**D**}.

MWNT-Based cathode tubes for elements of large-area outdoor displays were produced in Japan.[402–404] The tube diameter and length were 20 and 74 mm, respectively. The devices exhibited stable electron emission and long lifetimes (continuous glow over a period of 3 months). Their brightness was twice as high as that of conventional hot-cathode devices.

The results of research into NT-based field emitters for CRT displays and light sources carried out in Japan were reviewed by Saito and Uemura.[405]

A flat plane display with a brightness of up to 800 cd cm^{-2} at 5 V μm^{-1} was fabricated in Taiwan.[406] A method for fabrication of field emitters from SWNT bundles was developed by researchers from the PR China.[407]

Nanotubes represent a new kind of goods on the world market. The emission properties of commercially sold SWNTs and MWNTs were studied by Monteiro *et al.*[408]

An SWNT-based display 11.4 cm in diagonal with a brightness of 1800 cd cm^{-2} was fabricated (see Ref. 409). In 1998 and 1999, Ulvac Japan Ltd. and ISE Electronics Corp. (both from Japan) and Samsung Corp. (South Korea) demonstrated elements of CRT and prototypes of MWNT-based displays (these materials can be accessed *via* the Internet at URLs http://www.jnmr.com/intro/nanotubes.html and http://www.itron-ise.co.jp/english/nano/). In the late 1999, ISE Electronics Corp. had test-produced these display devices (this material can be accessed *via* the Internet at URL http://www.jnmr.com/intro/nanotubes.html). Research at Samsung Advanced Institute of Technology led to development of an NT-based 9 inch colour flat panel display with a resolution of 576 × 242 lines (this material was presented by J M Kim at the American Physical Society Conference in March 2000 and can also be accessed *via* the Internet at URLs http://www.eps.org/aps/meet/MAR00/baps/abs/S2090003.html and http://fuji.stanford.edu/seminars/spring00/slides/kimSlides.html). Samsung Corp. plans to start commercial production of NT-based colour displays in 2001–2002.

Large-scale industrial production of NT-based displays requires solving two major problems, *viz*., to make NTs cheaper

and to develop methods for fabrication of large-area NT-based emitting surfaces with uniform nanotube characteristics.

Nanotube-based field emitters can find applications not only in flat panel displays, but also in production of light sources, in such devices as vacuum pressure probes, microtriodes, klystrons, *etc*.

c. Memory devices

No NT-based memory devices have been fabricated so far. Nevertheless, some proposals that NTs can be used for this purpose have been made. Such memory elements can consist of, *e.g.*, $K@C_{60}^{+}$ complex encapsulated into short, closed 1.4 nm-diameter (10,10)-NTs (any other alkali metal can be used instead of K). The $K@C_{60}^{+}$ 'molecule' can change the equilibrium position from the 'bit 0' to the 'bit 1' ends of the capsule under the action of an electric current. The time taken to reach the opposite end of the NT is only 4 ps, which is ten times shorter than the switching time of conventionally used memory elements.[410] The system resembles a kind of nanoscale 'abacus' or a nanoscale 'shuttle'. The authors of this study[410] have discussed some approaches to large-scale fabrication of these structures; however, solving this problem faces great difficulties at present.

Nanotube structures with encapsulated neutral C_{60} molecules (nanoscale 'peapods')[31] are formed by cyclic raising and lowering the temperature. The yield of these structures can be increased by varying the reaction conditions.[33] It was stated that this method allows mass production of the nanoscale 'peapods'.[34]

Prospects for fabrication of NT-based memory devices for molecular computers have been outlined.[411] Memory arrays built of NTs are expected to store 10 000 to 30 000 times larger amounts of information and operate 1000 to 10 000 times faster than modern memory chips.

d. Nanolithography

Currently, intensive research has been carried out into fabrication of semiconductor devices with a characteristic size of 100 nm and less. Optical lithography using sources of short-wave UV radiation (λ = 193 nm) is limited by the lack of optically transparent materials at wavelengths shorter than 190 nm. This requires development of alternative methods for nanoscopic etching that use, *e.g.*, a new type of microscope probes.

The invent of scanning tunnelling microscope (STM) dates back to the early 1980s. The AFM, which is based on measurement of the adhesive force, is known since 1986. Usually, the STMs provide better resolution than the AFMs which are capable of operating without conducting substrate. The invention of the STM and AFM offered the possibility of manipulating individual atoms and molecules and moving them nanometre-scale distances.[412–420] The greatest drawback of both types of instrument consists in frequent metallic probe tip 'crashes' with the surface. The probe lifetime can be extended by using a carbon NT attached to the end of a silicon cantilever as the probe tip.[421]

Molecular dynamics simulations demonstrated that diamond surface can be selectively etched using an NT tip with attached C_2 groups.[422] It was concluded that NTs with the unmodified ends with strong covalent C–C bonds can be used for atomic-scale etching of semiconductor surfaces with relatively weak bonds (*e.g.*, Si and Ge). Another simulations performed by the same method revealed the possibility of nanoscale etching and indentation of the Si(001) surface using NT ends (this material can be accessed *via* the Internet at URL http://www.foresight.org/Conferences/MNTs6/Papers/Dzegilenko/).

Local anodisation of hydrogenated Si(100) surface and lithographic transfer of silicon dioxide in the form of lines 10 nm wide at a speed of $\sim$0.5 mm s^{-1} in the experiments with an AFM equipped with a MWNT probe tip were reported.[423] The lithographic writing speed achieved using the MWNT probe tip was 5 times higher than with other probes. It was shown that the NT tips present a solution to the tip-wear problem and are impervious to breakdown in high electric field. Theoretical foundations of the method were considered.

Nanoscale lithography experiments with polysilane films using an STM equipped with an NT probe tip showed that the NT tip provides higher resolution, larger groove depth-to-width ratio at higher scanning speeds and extended tip lifetime than the probe tips made of other materials.[424]

Impressive experiments were carried out on the manipulation and deposition of individual atoms on a surface using the STM probe tip[425,426] and the possibility of atomic-level modification of nanostructures was shown.[415] This gave an impetus to the study by Král and Tománek[427] who tried to eliminate the major drawback of modern STM, that is, manipulation of a single atom. They theoretically substantiated the possibility of design of a 'molecular pump'. Open NTs serve as ideal material for such a 'pump'. The atoms filling the inner cavities of NTs can be pumped through the NTs by irradiating with two pulsed lasers.

New lithographic methods are expected to provide fabrication of ICs with the circuit density 8 times higher and performance 16 times higher than those of the ICs produced using optical lithography technique by 2004.

e. Amplifiers and generators for cell phone communication

Using the ability of NTs to emit electrons upon application of relatively low voltages (this requires small energy expenditures but the current density remains high), researchers from the North Carolina University (USA) developed an NT-based microwave generator.[428] This property of NTs can find applications in wireless communication devices. Usually, cell phones generate weak signals that are amplified at a central office. Unique properties of NTs allow production of the central offices characterised by smaller size and longer service life. A prototype of such central office has been developed.

The property of NTs to change their electric characteristics under the action of mechanical stress was proposed for use in a new generation of phones.[428]

f. Other applications

Tsukagoshi *et al.*[429] obtained rather encouraging results concerning the use of NTs for design of electron spin devices. Injection of spin-polarised electrons into MWNTs resulted in coherent electron spin transport.

Nanotubes have unusually high thermal conductivity which approaches or even reaches some record values.[430–433] This suggests the possibility of using NTs as heat sink for ICs and electric motors (this material can be accessed *via* the Internet at URL http://composite.about.com/industry/composite/library/PR/2000/blupenn1.htm). According to model calculations,[430] individual nanotubes in NT bundles interact with one another rather weakly and thermal vibrations occur solely along the NT axis.

Prospects for design of an NT-based molecular-scale digital computer and a new chemical approach to production of ICs have been discussed (this material can be accessed *via* the Internet at URL http://marble.he.net/~foresite/Conferences/MNT7/Abstracts/Ellenbogen2/index.html).

To reduce the size of electrical contacts in future ultraminiature ICs and electromechanical nanosystems, researchers at ORNL proposed to replace the wires and pins by NTs placed both on and off the chip. It is assumed that carbon NTs outside the chip will communicate with the on-chip NTs through field-emitted electron beams (this material can be accessed *via* the Internet at URL http://www.ornl.gov/ORNLReview/rev32_3/brave.htm).

Nanotube-based electrodes can find efficient application in gas-discharge tube protector units which are used in telecom network interface device boxes and central office switching gears to provide protection from lightning and AC power cross faults. Tests showed that characteristics of experimental NT-based gas-discharge tubes (mean DC breakdown voltage and breakdown

reliability) were better than those of commercial products (this material can be accessed *via* the Internet at URL http://www.eps.org/aps/meet/MAR00/baps/abs/S4890/html; communication M10.003).

3. Fields of application of nanotubes in power engineering

a. Lithium batteries

Research on current sources with high specific (per unit mass and unit volume) energy capacity is an important avenue of development of 'small' power engineering. Here, the most widely used are lithium current sources in which lithium is intercalated into graphite or other carbon materials (see, *e.g.*, Ref. 434). Nearly immediately after their discovery, fullerenes appeared to be the subject of intensive studies in this field. This also holds for NTs. If the capacity of graphite is limited to one lithium atom per six carbon atoms, the capacity of NT bundles must be higher, since lithium atoms can fill both the intertubular space of the NT bundles and the inner cavities of individual NTs. According to *ab initio* calculations, the content of lithium in SWNT bundles can be much higher than in graphite and correspond to the composition LiC_2.[435]

Intercalation of lithium and other alkali metals follows the same pattern and is accompanied by charge transfer without structural distortions. Single-walled NTs recovering their initial structure after de-intercalation similarly to NT bundles seem to be of greatest interest for the use in rechargeable batteries.[174]

Single-walled NT bundles were intercalated with Li not only by vapour transport, but also electrochemically.[178,436] The limiting intercalation degree corresponded to the composition $Li_{1.7}C_6$, which is much higher than the ideal value for graphite and that determined for MWNTs (LiC_6).[437–439] The irreversible specific capacity was as high as 952 mA h g^{-1}. The reversible specific capacity was measured to be 447 mA h g^{-1}; however, it reduced to 237 mA h g^{-1} and lower after fifth charge–discharge cycle. For comparison, the reversible capacity of lithium cells with graphite electrodes lies between 280 and 330 mA h g^{-1} (see Ref. 434).

As a rule, electrochemical intercalation of lithium into SWNT bundles is performed using a pressed NT mat placed on a platinum plate as the working electrode and a 1 M $LiAsF_6$ solution in ethylene carbonate and diethyl carbonate (1 : 1) as electrolyte.

Heat treatment of NTs improves their texture and reduces the oxidation–reduction overvoltage difference but has a drawback consisting in reduction of capacity.

High intercalation degrees (up to $Li_{2.7}C_6$) were achieved using impact grinding pre-treatment of purified SWNTs followed by electrochemical intercalation in 1 M $LiClO_4$ solution in a mixture of ethylene carbonate and dimethyl carbonate taken in equal volumes.[161] Mechanical treatment for some time resulted in the loss of ordering of the NT bundles and in an increase in the average intertubular spacing. However, the mechanism of such a strong enhancement of the NT capacity to lithium remains unclear. Most likely, the metal atoms fill not only the intertubular space, but also the inner cavities of NTs.[161]

The metal content in the product can be increased by increasing pressure.[440] Intercalation of lithium into NTs at high pressures resulted in a material with the atomic ratio Li : C = 2. The NTs retained their structure and the lattice parameter along the *c* axis increased to 0.411 nm.[441]

Another method involves coating of NTs with copper, their oxidation in air for 12 h at 160 °C and subsequent electrochemical intercalation with lithium.[442] Carbon NTs obtained in this manner can reversibly store the amount of lithium (per gramme of carbon) corresponding to a capacity of 700 mA h (*cf.* 268 mA h per gramme of CuO for composites). Intercalation of lithium into and deintercalation from CuO require applying a voltage ranging from 1.7 to 1.0 V and from 2.3 to 2.5 V, respectively (*vs.* lithium electrode). The reactions proceed by the following mechanism

$$CuO + x\bar{e} + x\,Li \longrightarrow CuOLi_x.$$

Yet another, relatively recently proposed route to enhancement of the capacity of lithium current sources consists in the use of membranes with vertically aligned NT arrays as anodes. (The NTs were prepared by template synthesis followed by removal of the template, as shown in Fig. 2). Che *et al.*[374] used a 60 μm thick Al_2O_3 template with 200 nm pores. Nanotubes were deposited within the pores. The NTs were held together by the thin layer of carbon precipitate formed on the external surface of the template. Multistage treatment of the product followed by dissolution of the Al_2O_3 template resulted in a pure carbon NT membrane consisting of the NTs of relatively large diameter which replicated the structure of the template. The inner cavities of this membrane were filled with iron catalyst (from solution), the CVD procedure was repeated to obtain thin helical NTs inside the large-diameter NTs and then the system was electrochemically intercalated with lithium. It was found that the well-developed membrane surface allowed the capacity to lithium to be nearly doubled as compared to that of a membrane without 'internal' NTs.

The use of NTs in lithium current sources is thought to be promising. Recently fabricated SWNT- and MWNT-based Li anodes are characterised by a discharge capacity of 640 and 385 mA h g^{-1}, respectively, which is much higher than the parameters of industrially produced samples.

b. Hydrogen accumulators

The development of lightweight and safe systems for H_2 storage is necessary for wide use of highly efficient H_2–air fuel elements in, *e.g.*, transportation vehicles. According to calculations, for a car with rechargeable hydrogen 'reservoir' to travel 500 km, 3.1 kg of H_2 is required. To this end, the 'reservoir' must have a capacity of 62 kg m^{-3} and the concentration of H_2 in the hydrogen-saturated material must be at least 6.5% (these values represent the U.S. Department of Energy targets for hydrogen storage for fuel cell vehicles). Hydrogen fuel is more environmentally safe than hydrocarbon fuel, since the only combustion products are water vapour. For long, industry looked to hydride-forming metals and alloys as the basis for high-capacity and safe H_2 storage systems.[443] On the other hand, a number of studies on the use of fibrous and tubular forms of carbon and SWNTs has been published recently.[444–449]

The first experimental data on the hydrogen sorption on NTs were reported by Dillon *et al.*[444] in 1997. In studies of temperature-programmed desorption of H_2 from a material containing only 0.1% of SWNTs 1.2 nm in diameter and obtained by arc method in the presence of Co catalyst using the Siverts apparatus, they inferred that the adsorption capacity of nanotubes to hydrogen varies between 5 mass % and 10 mass % or 20 kg m^{-3} at −140 °C and 40 kPa. Since the measurements were performed for unpurified material, the authors had to make a far-reaching extrapolation to NTs of purity 99%, so the results obtained can hardly be considered precise. It was found that the adsorption capacity of NTs 2.0 nm in diameter (up to 50 kg m^{-3}) approaches the desired characteristics (Fig. 15).

Ye *et al.*[450] studied pristine SWNTs and found that hydrogen adsorption on the NTs was 8.25 mass % at 80 K and a pressure of 12 MPa. Single-walled NTs were prepared by laser-induced thermal synthesis in the presence of catalysts. Individual NTs were 1.3 nm while NT bundles were 6 to 12 nm in diameter. The specific surface area of the material was 285 m^2 g^{-1}. At pressures above 4 MPa, the SWNT material undergoes a transition to a new state of hydrogen coverage. Here, adsorption occurs not only on the external surfaces of the NT bundles, but also on the surface of individual NTs (according to calculations, the specific surface area of the NTs was 1600 m^2 g^{-1}). The cohesive energy of the SWNT bundles was estimated at 4.5 meV per carbon atom. The behaviour of sonicated material differs from that of the untreated material.

Bacsa *et al.*[451] prepared NTs with a specific surface area of 790 m^2 g^{-1} and suggested even higher adsorption capacity of their material.

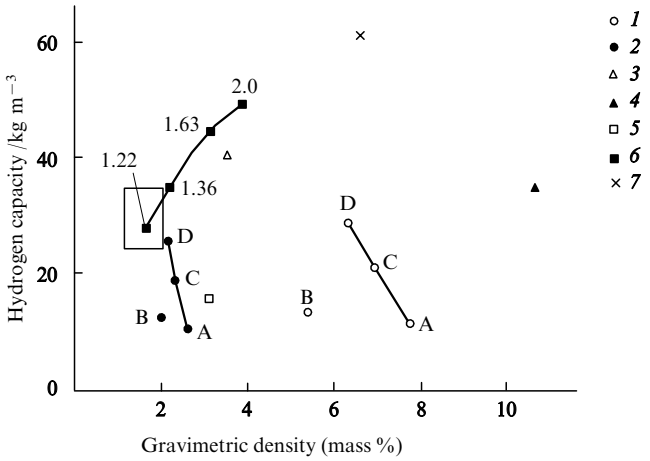


Figure 15. Characteristics of different materials as hydrogen accumulators.[444]
H_2 in the C/polymer composite cylinders at different pressures (*1*), H_2 in the glass fibre/Al composite cylinders at different pressures (*2*), H_2 produced in the reaction of Fe with H_2O (*3*), liquefied H_2 (*4*), H_2 on activated carbon (*5*), H_2 in SWNTs (figures denote the nanotube diameters given in nm) (*6*) and the region of desired parameters (*7*). The region of metal hydrides is shown within a rectangle. Pressure /MPa: 20 (A), 24.8 (B), 40 (C) and 60 (D).

Table 3. H_2 Storage properties of various systems.

Material	Max. mass % H_2	T/K	P /MPa	Ref.
Single-walled NTs (low purity)	5–10	133	0.040	444
Single-walled NTs (high purity)	8.25	80	7.18	450
Single-walled NTs (50% mass pure)	4.2	300	10–12	449
Nanofibres (tubular)	11.25	298	11.35	446
Nanofibres (herringbone)	67.55	298	11.35	446
Nanofibres (platelet)	53.68	298	11.35	446
No structure given	0.4	298–773	0.101	447
Graphite	4.52	298	11.35	446
Li–NTs	20.0	473–673	0.101	447
Li–graphite	14.0	473–673	0.101	447
K–NTs	14.0	<313	0.101	447
K–graphite	5.0	<313	0.101	447
FeTi–H	<2.0	>263	2.5	455
NiMg–H	<4.0	>523	2.5	456
Sorbent saturated at low temperature	~5	~77	2.0	456
Octane gasoline [a]	17.3	>233	0.1	456

[a] Given for comparison.

Single-walled NTs of relatively large diameter (1.85 nm) were synthesised by the arc technique. The reaction was performed in an apparatus with a rotating 400 mm-diameter cylindrical anode with drilled radial openings filled with graphite powder and a catalyst.[448] To obtain cheaper NTs, the synthesis was carried out in a H_2–Ar rather than H_2–He mixture using S-containing additives. Nanotubes were produced at a rate of several grammes per hour.

Specially treated NTs 1.85 nm in diameter can store up to 4.2% of H_2 with respect to their own mass (the atomic ratio H : C = 0.52) at room temperature and a pressure of 10 MPa. It was found that ~80% H_2 can be desorbed and room temperature at atmospheric pressure. Complete desorption of H_2 requires some heating of the material.[449] The samples under study were pre-annealed at 773 K for 2 h, which favoured enhancement of the adsorption capacity. The capacity was nearly unchanged after four charge–discharge cycles. The NT content in the material was varied between 50% and 60%, so its purification was suggested to result in considerable enhancement of the adsorption capacity.

Chen *et al.*[447] reported sensational results, according to which lithium-doped MWNTs can adsorb up to 20% of H_2 with respect to their own mass over a period of 2 h at 380 °C while the adsorption capacity of potassium-doped MWNTs can be as high as 14% at room temperature. According to calculations, a 20% adsorption corresponds to 3 hydrogen atoms per carbon atom while the fuel necessary for a car to travel 500 km can be stored in a 18 litres 'reservoir' of carbon NTs (this material can be accessed *via* the Internet at URL http://www.nus.edu.sg/INTsRO/newsletters/issue_20/CurrRes.htm). The results obtained by Chen *et al.*[447] were considered doubtful.[452] Indeed, attempts at reproducing these results using NTs produced by the same methods inferred that such a large increase in mass was due to the presence of water vapour in H_2.[453] Alkali metals do enhance the adsorption capacity of NTs, but to a much lesser extent than was reported by Chen *et al.*[447]

Great interest was attracted to the study by Rodriguez *et al.*[446] who synthesised graphite fibres capable of storing up to 67% of their own mass of H_2, which corresponds to a H : C ratio of 24. These results met initially with wide spread scepticism, since no experimental details were reported. Park *et al.*[454] to some extent clarified the situation. Unusual behaviour of the fibres was related to their structure with a specific surface area of 1000 $m^2\ g^{-1}$ and specific volumes of microscopic and macroscopic pores of 0.36 and 0.41 $m^2\ g^{-1}$, respectively. However, this issue requires further investigations.

The data listed in Table 3 characterise the hydrogen storage properties of NTs and other hydrogen accumulators and the state-of-the-art in this field.

Hydrogen storage in NTs was reviewed by Fischer[457] and Tarasov *et al.*[458]

Electrochemical storage of hydrogen in unpurified MWNTs 2 to 15 nm in diameter and SWNTs 0.7 to 1.2 nm in diameter was studied.[459] Relatively reliable results were obtained only in the experiments with SWNTs whose specific energy capacity was found to be rather high (110 mA h g^{-1}, or 0.39%). The reaction proceeded reversibly.

Electrodes with open SWNTs provided reversible electrochemical charging of up to 2.9 mass % of hydrogen, which corresponds to a specific energy capacity of up to 800 mA h g^{-1} (see Ref. 460). As the charge current changed from 10 to 100 mA, the capacity changed only by 50 mA h g^{-1}. This differs NTs from metal hydrides whose specific capacities are strongly dependent on the charge current. The maximum specific capacity was achieved after 20 charge–discharge cycles and was kept constant for the next nearly 50 cycles.

A large number of theoretical studies on H_2 adsorption has been published. Most of them were cited by Park *et al.*[454] Pederson and Broughton[461] were the first to propose that NTs can be filled with gas molecules due to the action of capillary forces.

The results of model calculations of H_2 adsorption[199] differ appreciably from experimental data. Insignificance of quantum effects at temperatures above 50 K and low hydrogen coverages of the NT surfaces was pointed out. The calculated storage capacities were found to be lower than those obtained from gravimetric measurements.[462–464]

Hydrogen adsorption in SWNT bundles was calculated.[465] The bundles consisted of square arrays of SWNTs 0.7 to 1.96 nm in diameter with an intertubular spacing of 0.334 nm. The effect of variation of the intertubular spacing on the NT storage capacity was studied taking 1.174-nm-diameter NTs as an example. It was shown that the highest H_2 storage capacity at room temperature

(10.7 kg m^{-3}) is achieved at an intertubular spacing of 0.7 nm. However, the manner in which the intertubular spacing in the NT bundles can be changed remains unclear.

The possibility of electrochemical storage of H_2 in SWNTs was confirmed by Lee *et al.*[466,467] who also performed a theoretical study of the process. Several adsorption sites in and on the SWNTs were found. According to Raman spectroscopy data, the inner NT cavities are filled with H_2 molecules. Molecular dynamics simulations showed that the highest hydrogen storage capacity of (10,10)-NTs is 14.3 mass % (160 kg H_2 m^{-3}) and increases linearly with the NT diameter. Multi-walled NTs exhibit a lower hydrogen storage capacity. In this case, hydrogen is adsorbed on the external MWNT surfaces and their capacity is independent of diameter.

Based on the above-mentioned experimental results, yet another group of theoretical studies was carried out. For instance, it was found that the desired 62 kg m^{-3} capacity (3.1 kg of H_2) of the NT 'reservoir' at 77 K can be achieved using SWNTs 0.6 nm in diameter at an intertubular spacing greater than 1.0 nm. Nanotubes carrying an electric charge were predicted to exhibit an enhanced hydrogen storage capacity (by 10% to 20% at 298 K and by 15% to 30% at 77 K).[468]

Williams and Eklund[469] attempted to bridge the gap between the results of theoretical and experimental studies. They pointed to the fact that all calculations performed so far used a model of infinite three-dimensional SWNT crystal lattice, whereas electron microscopy data show that SWNT bundles form a close-packed triangular 'honeycomb' lattice and have finite diameters and length. Mention was also made of inadequacy of the approach relating enhanced adsorption to arbitrarily changed symmetry or increased intertubular space.

c. Electrolytic capacitors

Thin NT films coated on metallic surfaces are of considerable practical interest for production of supercapacitors characterised by high capacity and the ability to survive a large number of charge–discharge cycles. The capacity of capacitors with an electrical double layer is known to increase linearly with the specific surface area that is rather large in the case of NTs (more than 300 m^2 g^{-1}).[470] In addition, it is important to use low-resistance electrode materials and to know the resistance of the electrolyte in the porous electrode structure. Carbon or graphite provide no possibility for fabrication of highly porous, 'mat'-like electrodes, which is necessary for obtaining an optimum pore structure; however, this can be readily done using NTs. The specific capacitance of catalytically grown NTs of size $\sim$8.0 nm in 38% H_2SO_4 reaches 102 and 49 F g^{-1} at 1 and 100 Hz, respectively. A single cell device had a power density exceeding 8000 W kg^{-1} (see Ref. 471).

Cyclic voltammetry measurements[472] revealed an effective capacitance of 283 F g^{-1} at 0.5 V (*vs.* silver reference electrode), which is twice as large as the maximum value for carbon electrodes in non-aqueous media (120 F g^{-1}). The material was stable on potential cycling and no differences were observed after continuous cycles over 30 min at 50 mV s^{-1}.

Capacitors with NT block electrodes and specific capacitance of 90 F g^{-1} were produced.[473]

Nanotube-derived capacitors can be used for laser power supplies, wrist watches, flash lamps, starters for electric motors, *etc.* They can also find military applications in, *e.g.*, bird- or insect-size reconnaissance airborne vehicles.[470]

4. Fields of application of nanotubes in analytical instruments

a. Sensors

Single-walled NTs are rather sensitive to gas atmosphere and can change their electrical resistance and thermal emf upon adsorption of N_2 or He.[212] This was the starting point for work on an 'electronic nose', or a chemical gas sensor.

SWNT-Based chemical NO_2 and NH_3 sensors are characterised by extremely short response time, thus being different from conventionally used sensors.[474] The sensitivity of the new sensors is three orders of magnitude higher than that of standard solid-state devices. A 0.02% concentration of NO_2 increases the electrical conductivity by 3 orders of magnitude after 10 s exposure, while exposure to 1% NH_3 decreases it by two orders of magnitude after 2 min. To reset the new sensors, they must be heated because of the low relaxation rate at room temperature. These sensors are very small (their size does not exceed several micrometres), simple in design (an NT connecting two conductors), cheap and operate at room temperature. A CO_2 sensor has been developed (this material can be accessed *via* the Internet at URL http://www.newscientist.com/ns/19991225/newsstory13.html). It should be mentioned that providing the possibility of sensing particular gases in complex mixtures selectively remains a moot question.

Nanotubes are thought to be of use for development of miniature sensors that each soldier might carry to detect poison gas or biological weapons (this material can be accessed *via* the Internet at URL http://www.post-gazette.com/healthscience/1999101nanotubes1.asp).

Frequency shift in the Raman spectra upon immersion of SWNTs in various liquids can find practical application in the development of sensors to test liquids. The frequency shift magnitude depends on the surface tension of a particular liquid, which can be used for the determination of its chemical composition.[249,475]

Construction and characteristics of items fabricated from individual MWNTs were reported.[476] Nanotubes 80 to 120 nm in diameter and 15 to 50 μm long were attached to a platinum tip using conducting epoxy resin. The NT side walls were insulated with polyphenol. Cyclic voltammograms measured at different electrode immersion depths in electrolyte solutions were obtained.

Nanotubes can be used as electrode material.[477] Redox-proteins immobilised on the surface and inside NTs exhibited well reproducible cyclic voltammograms. Immobilisation of DNA treated with I_2 and $[Pt(NH_3)_2]^{2+}$ and other proteins on NTs was also carried out.[478]

The possibility of attachment of metal porphyrins (including enzymes) to NTs allows fabrication of biosensors for studying different biomolecules and other biological objects. In particular, a proposal was made that NTs can be used as microelectrodes for the determination of glucose and cholesterol concentrations. The use of NTs can lead to basic change in the blood count procedure, so a drop will be enough to perform complete blood count over a very short time. The results reported by Balavoine *et al.*[479] who obtained ordered helical shells of protein molecules on the NT surfaces can be considered as the first step towards the development of new biosensors.

b. Microscope probes

Usually, STM probes are made of tungsten or platinum while AFM cantilevers are made of silicon or Si_3N_4. Typically, the radius of curvature of the AFM cantilever tips varies between tens and hundreds of Ångström. The use of NTs as probe tips was first reported by Dai *et al.*[421] who attached SWNTs to a pyramidal silicon cantilever, tested the device and obtained encouraging results. The use of chemically inert, conducting, hydrophobic, thin and flexible NTs makes the research process more simple; allows penetration into narrow grooves; improves resolution and provides the possibility of performing non-destructive studies of delicate biological objects.

A detailed instruction for attachment of NTs to commercial STM probes was posted on the Internet at URL {[http://cnst.rice.edu/mount.html]**D**}.

Nanotube growth immediately on commercial STM probes by pyrolysis of hydrocarbons was reported.[480–483] This method is considered to be much more simple than attachment of arc-grown NTs. Yet another technique consists in attachment of NTs in an electric field.[484–486] However, the simplest and most closely related to large-scale production conditions method[487] involves

a combination of (i) CVD of NTs on a special cartridge by catalytic pyrolysis [384] and (ii) transfer of the grown NT from the cartridge to the microscope probe tip in an electric field.

The properties of 'capped' NTs as materials for tunnelling microscope probes have been described by Harrison *et al.*[488] The radius of curvature of an SWNT probe tip is 3 to 6 nm (sometimes, even 0.2 to 0.5 nm), which is several times smaller than for conventional probe tips.[489]

Using an AFM with an NT probe tip, Choi *et al.*[490] obtained images of individual NTs on mica surface, while Zha *et al.*[491] studied chromium-filled NTs with an STM.[491]

Wong *et al.*[89, 90, 92, 492] oxidised NTs in air at 700 °C (98% of the carbon material was burnt out), functionalised their tips with carboxylic groups and obtained world's first chemically sensitive probe microscope capable of analysing different substances at the molecular and atomic levels. Then they performed amino, hydrocarbon and bioactive functionalisation of the carboxy-modified probe tips by the formation of chemical bonds between CO_2^- groups and one of the amino groups of ethylenediamine molecule, amide bonds with benzylamine molecule and amide bonds with biotin derivatives, respectively. The first (carboxy-functionalised), second and third probe tips possessed acidic, basic and hydrophobic properties, respectively. The fourth probe tip was sensitive to streptavidine. In principle, CO_2^- groups can form bonds with a broad spectrum of functional groups, which allows fabrication of probe tips for various applications.

Wong's 'constructions' exhibit some advantages over the previously used probes. The point is that earlier functionalisation of the Si_3N_4 or SiO_2 cantilevers resulted in attachment of functional groups not only to the tip, but also to the side walls, which damaged the objects under study. In contrast to this, no damages were observed in the experiments with NT tips since the functional groups were attached only to the 'cap'. In addition, NT probes are characterised by small effective radius and provide higher resolution. Finally, 1.4-nm-diameter (10,10)-NTs contain only 20 atoms at the open end, so it is an easy matter to choose the conditions for fabrication of a probe tip functionalised with a single group with known structure and orientation even at random distribution of the NTs with different number of carboxylic groups at the end.

Specifically functionalised NT probe tips can be used for selective removal of atoms from the surface.

Probe microscopes were used to obtain the first images of DNA molecules.[489] Microscopes with NT probe tips allow shortening the time taken to analyse large DNA molecules.[493]

Atomic force microscopes with NT probe tips were used for the determination of the structure of protein complexes [494] and for manipulating DNA molecules. At particular voltages, the DNA molecules were adsorbed on NTs and arranged on their surfaces in a predetermined manner (this material can be accessed *via* the Internet at URL http://www.eps.org/aps/meet/MAR00/baps/abs/S4890/html; communication M10.010). A well-resolved image of right-hand helical DNA molecule has been reported.[495]

Nanotube-modified cantilevers allow improving the resolution of electrostatic force microscopes.[496]

Improved AFMs with NT probe tips can be used in studies of both rigid and soft surfaces in aqueous solutions. According to recent predictions, these microscopes will serve as the basis for a breakthrough in biological studies.[497]

Nanotube probe tips can also be used as the 'reading' probes in memory storage devices of supercomputers. A possible candidate would be a system consisting of layering H and F atoms on a diamond surface and a pyridine molecule attached to the probe tip end. Theoretically, the system can store 10^{15} bytes cm^{-3} (this material can be accessed *via* the Internet at URL http://www.msu.edu/~hungerf9/nanotube.html).

5. Nanotubes as catalyst and sorbent supports

The idea of using NTs as catalyst supports was proposed nearly immediately after the discovery of this form of carbon.[498, 499] This application of NTs is based on their chemical stability and well-developed surface. Catalysts can be obtained by the filling of the inner cavities of NTs or in the course of their decoration or, in particular, in the course of the NT synthesis.

Only one study concerning SWNTs was cited in a short review on the application of fullerenes and NTs as catalyst supports.[500] After long-term storage in hydrogen at 673 K a material grown by arc method in the presence of cobalt and platinum exhibited high selectivity in the liquid-phase hydrogenation of cinnamaldehyde.[501]

Multi-walled NTs were also studied as catalyst supports. A Ru catalyst coated on arc-grown MWNTs with a specific surface area of 27 $m^2\ g^{-1}$ allowed an increase in the yield of hydrocinnamic alcohol obtained by hydrogenation of cinnamaldehyde to 80%. It was found that reduction selectivity increased from 30% – 40% to 92%.[502] A nanotube-supported rhodium catalyst was found to be efficient in the thermal decomposition reaction.[503] Complete decomposition of NO occurs at 600 °C on NTs without catalyst, at 450 °C on NTs containing 1 mass % Rh and at 300 °C on the catalyst pre-treated with H_2 at 300 °C or higher temperatures. After 2 h exposure to NO at 500 °C the Al_2O_3 – Rh (1%) catalyst contained rhodium only in the form of Rh_2O_3, while the NTs – Rh catalyst contained metallic Rh (8 nm particles).

The efficiency of different supports was compared taking the reaction of catalytic hydroformylation of propene as an example.[133] It was found that MWNT-supported ruthenium phosphine complex is not only much more active than other supports, but also exhibits high regioselectivity towards butyraldehyde (the reaction product) despite relatively small specific surface areas (155 and 237 $m^2\ g^{-1}$) and pore volume (0.46 and 1.33 $cm^3\ g^{-1}$) and relatively small pore diameter (3.2 – 3.6 and 2.4 – 3.2 nm) of the MWNTs used. Nanotubes were compared with supports characterised by much larger specific surface area (up to 1210 $m^2\ g^{-1}$, a carbon molecular sieve TDX-601), larger pore volume (up to 1.66 $cm^3\ g^{-1}$, a polymeric support GDX-102), and a larger (20 – 100 nm, GDX-102) or smaller pore diameter (1.4 – 2.0 nm, activated carbon).

Efficient catalysts were obtained by filling the inner cavities of the above-mentioned carbon membranes (see Section VIII.3.a) [374] with catalytically active metals. For instance, solution-coated platinum enhanced the rate of electrocatalytic reduction of O_2, while a Pt – Ru mixture enhanced the reduction of CH_3OH, which means that these catalysts are promising to be used for fuel elements. A study of the electrocatalytic reduction of dissolved O_2 using NTs showed that the exchange current density in the H_2SO_4 solution (pH 2) was five times higher than in the reaction carried out on graphite. This suggests possible use of NTs in fuel batteries.[504]

The rates of electrochemical processes occurring at platinum- and ruthenium-coated NT electrodes are higher than at platinated glass electrodes.

'Nanohorns', a recently found kind of NTs, appeared to be an excellent adsorbent of liquid ethanol. (The properties of 'nanohorns' were studied by Murata *et al.*[505]). The oxygen adsorption capacity of 'nanohorns' is 3.5 times higher than that of other forms of carbon with the largest specific surface area.[506] Moreover, 'nanohorns' catalyse oxidation of ethanol into acetaldehyde.

6. Application of nanotubes in optical devices

Molecules with high third-order optical nonlinearity and second-order hyperpolarisability are considered promising for use in photonic devices, *e.g.*, optical switches, data processing systems, optical filters and sensors. However, most of the third-order nonlinear optical materials have low second-order hyperpolarisability. Exotic electronic structure of NTs allowed researchers to hope for their application in nonlinear optical devices.

A theoretical model for SWNTs was proposed by Xie.[507 – 511] who also reported a third-order optical nonlinearity in chiral carbon NTs.[512] Chiral NTs as nonlinear optical materials are

quite competitive with conducting polymers. Large nonlinear optical effects are typical of zigzag and B-(N-)doped NTs.[513]

Second-order hyperpolarisability of NTs was predicted.[514, 515] The optical properties of NTs are strongly affected by the NT symmetry, the presence or absence of the 'cap' and the number of constituent carbon atoms.[516]

A theoretical expression for the third-order nonlinear optical susceptibility of NTs, related to the third harmonic generation, was derived by Margulis *et al.*[517] who pointed out that the resonant optical susceptibility of NTs is several orders of magnitude higher than that of C_{60} or C_{70}.

The properties of SWNTs 1.3 nm in diameter and ~ 160 nm long in a DMF solution were studied.[518] The ultrafast second-order hyperpolarisability was estimated at 2.1×10^{-28} esu.

Absorbing cells filled with a suspension of SWNTs in water were used as protection from laser radiation.[519] The effect of optical limitation was observed at 1064 and 532 nm. It was found that an increase in the radiation intensity by three orders of magnitude can reduce the optical transparency by two orders of magnitude.

Due to their unique properties, SWNTs rank first as nonlinear optical switches among all the materials used in this field, though the mechanism of the phenomenon is still to be clarified. Studies on the optical limitation of SWNT suspensions in water, ethanol and ethylene glycol showed that the magnitude of the effect can differ substantially in different liquids.[520]

Multi-walled NTs also exhibit remarkable nonlinear optical properties[258, 521, 522] that are comparable with those of soot and C_{60} suspensions. This type of NTs combines the advantages of both soot and C_{60}. Similarly to soot particles, NTs are relatively large. Similarly to fullerenes, NTs can be readily modified by, *e.g.*, filling to acquire desired optical properties.

Third-order optical nonlinearity of MWNTs was measured experimentally.[523] However, more recently it was found that incorrect experimental design led to observation of unusually high and unstable nonlinear optical response.

Nanotubes are poorly soluble; however, their composites with polymeric matrices can be used for protection from laser radiation. Laser irradiated solutions of NT solubilised in poly(phenylacetylene) exhibited unusual behaviour, *viz.*, they turned opaque with an increase in the radiation intensity.[112] Nanotube additives preclude optical damage to the polymer even at such high fluences as 10 J cm^{-2}.

Soluble complexes of MWNTs with polyacrylic acid and surfactants exhibit nonlinear optical properties.[121]

Dispersions of NTs in ethanol can be used for alignment of NTs under the action of electric current; they possess anisotropic properties and can change the direction of polarisation of the incident laser beam.[524] Conclusions drawn by the authors of this study deserve further confirmations, since all the measurements were carried out using insufficiently purified material.

Nanotube-containing composites can find application in photoelectric (photovoltaic) devices and light emitting diodes (LEDs).[113, 114, 246] Filling conjugated polymers with fullerenes was shown to be promising in the early 1990s. More recently, NTs became the subject of research. For instance, attempts at fabricating LEDs with microfiltration-aligned NT layer have been undertaken. However, the method involving preparation of an NT film by centrifugation and subsequent coating of the NT film with a poly(*p*-phenylene vinylene) film led to the best results.[246] Multi-walled NTs on the surface of polymer films somewhat reduce photoluminescence. The efficiency of NTs as hole-collecting electrodes of photovoltaic devices appeared to be twice as large as that of standard indium–tin oxide electrodes (the quantum yield at 2.9 to 3.2 eV was 1.8%).

Thin films of this composite can be used as emitting layer of LEDs and glow at lower current densities compared to the untreated polymer.[113]

7. Molecular nanotechnology

Nanotechnology is a field in which unique properties of NTs can best be used. Molecular nanotechnology concerns fabrication of functional structures and devices by atom-by-atom or molecule-by-molecule assembling using programmed robots (assemblers) capable of self-replication. According to calculations, the mass of an assembler equipped with a molecular computer and actuator can be at most 10^9 amu (this material can be accessed *via* the Internet at URL http://www.public.iastate.edu/~bhein/FAQ.html). The assembly will occur consistent with the chemical laws; however, under conditions of 'position' synthesis, where an atom or a molecule is supplied exactly to the place, these laws act in another manner compared to conventional chemical reactions conditions; if necessary, the overcoming of activation barriers can be achieved by consuming mechanical energy supplied from outside.

After the invention of STM and AFM, molecular nanotechnology is no longer only a scientific concept. There remains only some disagreement about how long its development will take {[this material can be accessed *via* the Internet at URLs http://www.nanomedicine.Com/2.1.html]**D**, .../2.2.html]**D**, .../2.3.html]**D** and .../2.4.html]**D**}.

In 1998, Zivex LLC (USA) demonstrated the possibility of three-dimensional manipulating NTs inside a scanning electron microscope with a resolution approaching that of the scanning probe microscopes and near real-time video control. The development of this manipulator and especially its improvement to provide the possibility of simultaneous operation of several independent manipulators inside one microscope is a great stride in the development of nanotechnology.

Probe microscopes allow one to manipulate NTs and move ('push around') molecules over the surface. Using a 'nanoplotter', one can draw lines up to 30 nm wide. However, these devices have a strongly confined action range.

New possibilities for manipulating nanoscale objects and studying their properties are opened after the development of the scanning probe microscope with 'nanotweezers', that is, two tiny plates of gold separated by a thin glass layer and attached to the tips of 100-nm-diameter NTs.[525] By applying an electric field it is possible to close and open the NTs and to grab and move submicrometre-size clusters and nanowires. Nanotubes of smaller diameter should make it possible to manipulate objects only 2 nm in size, *i.e.*, single molecules and structures inside biological cells, thus modifying them.

Initially, the greatest interest of experts in nanotechnology was attracted to various organic substances, especially a number of products of biosynthesis. It is assumed that molecular computers will be the first commercial fruit of the development of nanotechnology {this material can be accessed *via* the Internet at URL [http://www.resonance-pub.com/e-print%201.htm]**D**}. Currently, more definite hopes are associated with fullerenes and especially NTs. In particular, severe requirements imposed on the chemical and thermal stability of structural elements of molecular machines for aerospace industry make the use of NTs for fabrication of these elements justified.

Experts at NASA's Research Center (Ames, USA) also point out that NT-based nanotechnology can provide a way to reduce the cost of space missions.[526–529]

Bearings, springs and gears are important components of future nanomechanical systems. Their development is one of the main research avenues.

In 1992, benzene was found to react with C_{60} by the 2,4-cycloaddition mechanism. According to calculations (1997), such reactions on the external side walls of NTs are possible. That is why one of the pioneering studies on the development of NT-based nanomechanical devices was concerned with molecular dynamics simulation of a NT-based gear with benzene gear teeth {see Ref. 530 and material posted on the Internet at URLs [http://www.nas.nasa.gov/Groups/Nanotechnology/publications/MGMS_EC1/simulation/]**D** and [...MGM_EC1/quantum/index.

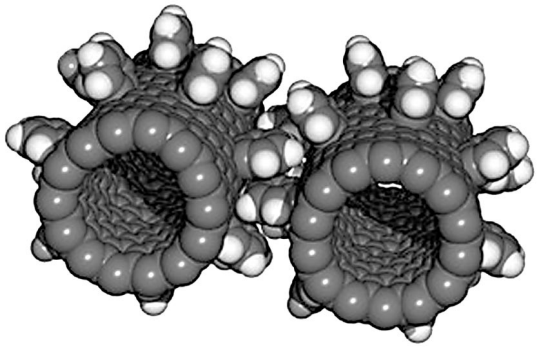


Figure 16. A nanotube gear with attached C_6H_6 molecules.

html]**D**}. Calculations were carried out for systems containing up to 2000 atoms. The angular momentum was transferred *via* two (14,0)-NTs 1.1 nm in diameter (Fig. 16). According to calculations, the gear could operate at frequencies up to 100 GHz *in vacuo* at room temperature. More recently, systems comprised of hundreds of thousands of atoms were calculated.

Other types of molecular gears were also calculated (this material can be accessed *via* the Internet at URLs http://www.nas.nasa.gov/Groups/Nanotechnology/publications/MGMS_EC1/simulation/paper.html and ...MGMS_EC1/index.html) and the behaviour of molecular devices in helium and neon atmosphere was studied. A phenomenological model of a laser-driven molecular motor was studied. The motor supplied power to a nanotube gear.[531]

Several video clips and animations illustrating the operation of various nano-gear devices can be accessed *via* the Internet at URL http://science.nas.nasa.gov/Groups/Nanotechnology/publications/MGMS_EC1/simulation/data/index.html.

Calculations of gears consisting of internal and external NTs were carried out. A concept of fullerene motor consisting of two concentric graphite cylinders (a shaft and a clutch) was proposed.

Possible conditions for coaxial arrangement of two NTs of different diameter (10 carbon atoms around the circumference of the shaft and 30 or 34 atoms around the circumference of the clutch) were calculated.[532]

Pioneering experimental studies attracted considerable attention. A team from the California University at Berkeley (USA) and Lawrence National laboratory (Berkeley, USA) managed to elongate MWNTs by pulling out the inner shells and then to shorten them by reducing the force exerted.[533] No indications of the 'nanospring' fatigue or wear were observed after 10 to 20 in/out cycles. The author of a popular essay on the subject predicts a passage from microelectromechanical systems that are on the scale of a human hair to nanoelectromechanical systems (NEMS) that are so small that 10 000 bearings for such systems can be stretched across the diameter of a human hair (this material can be accessed *via* the Internet at URL http://www.berkeley.edu/news/media/releases/2000/07/27_nano.html). According to expert evaluations, these systems will be developed in the nearest two years. At first, these will be hand-made devices and then some methods for their mass production are expected to be developed.

Based on the results of their studies on the behaviour of MWNTs under load, Yu *et al.*[534–536] pulled out inner shells of MWNT using an AFM and estimated the magnitudes of forces that act in this system. The proposed model of the process included the shear interaction, a specific type of 'capillary' effect (an interaction between two solids) and boundary effect (the influence of dangling bonds at the end of the inner NT 'immersed' in the outer shell).

The development of NT-based nanotechnology is associated with the breakthrough studies on nanolithography,[423] development of 'nano-fountain pen',[427] fabrication of functionalised probe tips and theoretical investigation of selective removal of hydrogen atoms from diamond surface.[422]

A rather large number of communications on NTs were reported at the 8th Conference on molecular nanotechnology held in the USA in November 2000 and called 'foresight'. In particular, new results were obtained on the character of conductivity in the 'arm-chair' NTs (http://www.foresight.org/Conferences/MNTs8/Abstracts/White/index.html); on the possibility of fabricating all-carbon electronic devices (.../Fuhrer/index.html); on the application of SWNTs of different chemical compositions (including metal-doped NTs) for fabrication of ICs (.../Darsey/index.html); on the stability of composite (cluster-type) structural elements made of NTs and diamond; on the possibility of fabricating heterojunctions for nanoscale logical and memory devices and NT-based field emitters 'capped' with diamond (.../Shenderova2/index.html); on theoretically studied gas separation processes using NTs and on the effect of NT filling with gases and C_{60} molecules on the mechanical properties of the NTs (.../Sinnott/index.html); on the thermodynamic properties of polyatomic liquids inside NTs and on the stability of NTs in aqueous solutions (.../Walther/index.html); on the quantum-mechanically studied effect of the surface curvature on the reactivity of NTs and fullerenes (.../Srivastava/index.html).

A recently published short review 'Carbon nanotubes. From macromolecules towards nanotechnology' [537] contains almost no information on applications of NTs in nanotechnology.

IX. Conclusion

Nanotube chemistry becomes a rather large division of general chemistry. Currently, it includes inorganic, colloid, polymer, physical and analytical chemistry of nanotubes (analytical chemistry of NTs also includes sensorics, the subject of which is development of chemical and biochemical sensors). Nanotube chemistry is closely related to nanotube physics, materials science and quantum chemistry. Some problems of NT chemistry are common to electronics and photonics.

Nanotube chemistry is also related to biochemistry. Some of the potential fields of application of NTs in biology were pointed out by Guo *et al.*[478] These are vessels for pharmaceuticals, biomimetic systems, which simulate biological objects and processes, catalysts prepared from immobilised enzymes, sensors, selective electrodes, biomolecule sensors, *etc*.

Studies on NT filling with various compounds can lead to applications of NTs as specific type of chemical reactors. One can expect that chemical reactions in the NT cavities will proceed in a significantly different manner compared to processes that are on different scale, since even such phenomena as melting of crystals and crystallisation of liquids or glasses inside NTs are characterised by some salient features.[538–540]

Nanotube chemistry is expected to become an integral part of nanotechnology which undergoes rapid development. Close relation between methods for fabrication of devices incorporating NT-derived elements and nanotube chemistry is also evident. Many applied research avenues have demands for NTs with uniform structure and size, and require chemical modification of NTs, *etc*.

Nanotubes continue to surprise researchers by their unusual properties. Among new discoveries are, *e.g.*, the superconductor proximity effect (a change in the electronic properties of a conventional conductor in the immediate vicinity of a superconductor);[541] superconductivity in $\sim$1-nm-diameter NTs at 4 K; magnetic flux trapping by a MWNT 'forest';[542] and oriented growth of SWNTs prepared by catalytic pyrolysis of CH_4 on the surface of single-crystalline Si.[543] For instance, NTs grown on the Si surface are oriented parallel to the surface in two perpendicular directions for Si(100) and in three directions at angles of 60° for Si(111). Probably, in the future this discovery will allow simplification of the fabrication process of hybrid NT structures and devices based on them.

However, the period when the results of almost all studies on NTs were considered fundamentally important (or at least of great importance) and when the search for new methods for the NT synthesis and the studies of their properties were the focus of research activity is now over. The focus of current research has been applied studies.

On the other hand, the synthesis of NTs with reproducible properties is still a challenge. For instance, a semi-continuous setup with a rotating anode for the arc synthesis of NTs has been reported;[448] an installation with rotating cathode for preparation of NTs under microgravitation conditions has been developed,[544] a method for continuous preparation of NTs using an arc immersed in liquid nitrogen was proposed,[545] a technique for the preparation of mostly two-walled NTs was developed;[546] and the performance of the setups for production of NTs by laser-induced thermal synthesis was improved and is now as high as 20 g per 24 h.

New synthetic approaches were developed. These are synthesis of NTs under hydrothermal conditions,[547] by exposure of a mixture of graphite and iron nanoparticles to atomic hydrogen,[548] by irradiation of amorphous carbon (fly ash) with Ar ions (this material can be accessed *via* the Internet at URL http://www.jnmr.com/intro/nanotubes.html) and thermal decomposition of aminoazines (in the presence of catalysts)[549] and saccharose.[550] A plasma jet method for the preparation of NTs was tested.[551] A joint team from Osaka Gas Co. (Japan) and Laboratory for New Technology developed a new technique for the synthesis of NTs, based on electron irradiation of a solid residue obtained by decomposition of fluorocarbons. This method allows the obtaining of a product containing $\sim$50% of SWNTs. The process requires the use of powerful electron accelerators and is expected to be readily scaled up (this material can be accessed *via* the Internet at URLs http://www.jnmr.com/intro/nanotubes.html and http://www.kippo.or.jp/news/1998-e/0617.htm).

Researchers from the Russian Federation were involved in the R&D of a method for the preparation of NTs by vaporisation of carbon at gas mixture pressures up to 1300 atm,[552] while researchers from Belorussia undertook considerable efforts aimed at developing the synthesis of NTs at temperatures below room temperature.[553]

However, the greatest advances were made in the preparation of NTs by the pyrolytic method, in particular, by decomposition of CO. The most remarkable is the development of a setup 'Marc II'[554] for production of highly pure SWNTs (up to 99%) by catalytic decomposition of CO. A jet of a mixture of CO and a metal carbonyl flows out of a high-pressure (tens of atmospheres) chamber and is heated to 900–1000 °C using a laser. The performance of the setup is expected to be $\sim$100 g of NTs per 24 h.[554]

A process of catalytic decomposition of CO under pressure (trade mark HiPCO^{TM}) was proposed to be of use for commercial production of SWNTs. It is expected that NTs will be produced at a rate of up to 10 kg per day in 2002 and at rates of hundreds or thousands of kilogrammes per day in 2003–2004 (this material can be accessed *via* the Internet at URL http://www.cnanotech.com; htth://carbonnanotech.com/CNI_ home.html).

A mixture of CO with 25% H_2 and iron carbonyl can be used for the synthesis of SWNTs at atmospheric pressure at 1100 °C (this material can be accessed *via* the Internet at URL http://fy.chalmers.se/f3a/Fullerenes/Nanotubes/projects/Ntproduction.html).

Catalytic pyrolysis of hydrocarbons at temperatures above 1000 °C was proposed to be a method for NT production at a rate of several hundreds of kilogrammes per day. The National Institute of Materials and Chemical Research (JNMR, Japan) and the Showa Denko Co. (Japan) work on a pilot plant since 1999 (this material can be accessed *via* the Internet at URL http://www.jnmr.com/intro/nanotubes.html).

Currently, various MWNT-based products are produced. These are NT powders, 'spaghetti', suspensions in various solvents and substrates covered with NT 'forest' arrays. An industrial process for the preparation of MWNTs of purity 95% is based on pyrolysis of hydrocarbons performed according to the method proposed by Ren *et al.*[392] The assortment of NTs and price lists are available in the Internet at URL http://www.nano-lab.com/SubPages/prices.html. In 1999, the market price was 100 USD per gramme for unpurified NTs and 1400 USD per gramme for purified SWNTs.[245] In March 2001, the price of purified SWNTs was reduced down to 60 to 100 USD per gramme (this material can be accessed *via* the Internet at URL http://www.carbolex.com/).

The pyrolytic method is expected to allow realisation of the idea of NT synthesis (build-up) on a 'seed' (a short NT with particular structure), thus presenting a solution to a complex problem of sorting the synthesised products by structure or shape (this material can be accessed *via* the Internet at URL http://cnst.rice.edu/VARENNA.html).

The idea of existence of a critical size for a catalytic particle is well known. It is believed that the use of catalytic particles of larger size makes preparation of NTs impossible.[555] This gave an impetus to search for novel approaches to development of catalysts. A JNMR's technology for mass production of MWNTs to be used in cathodes of television displays is based on the reversed micelle method. (this material can be accessed *via* the Internet at URL http://www.jnmr.com/dez/online/nlpage1013.html).

Flame preparation of NTs represents a kind of pyrolytic synthesis of NTs.[556–558] This process has much in common to an industrial processes of soot production and can be adapted to large-scale synthesis of NTs. Pyrolysis of sputtered solution of $Fe(C_5H_5)_2$ in C_6H_6 is yet another pyrolytic technique.[557]

In Russian Federation research into NTs are well-based (see, *e.g.*, recently published reviews[559, 560] covering studies in a close field of catalytic pyrolysis of hydrocarbons to prepare carbon filaments). A setup for catalytic decomposition of CO operating at a rate of kilogramme quantities of products per day was tested.

* * *

A number of studies on the subject of this review were published in the course of preparation of the manuscript. The most important and interesting results are outlined below.

A special issue of the journal 'Physics World'[561] dedicated to research into NTs was published.

Hirahara *et al.*[562] reported the synthesis of unique compound, $(Gd@C_{82})_n@$NTs. Structurally, it represents a nanoscale 'peapod' consisting of a SWNT with encapsulated electrically charged C_{82} 'peas' with a Gd atom inside each 'pea'. This 'doubly endohedral' substance was synthesised by the interaction of $Gd@C_{82}$ vapours with pre-open NTs. Electrical resistance measurements revealed electron transfer from the metal atom not only to the C_{82} molecule, but (tentatively) to the NTs. This opens new possibilities for modification of NTs and brings the advent of unique memory devices closer.

Two studies[563, 564] carried out independently concern chemical modification of particular sections of NTs, which can lead to the formation of intramolecular heterojunctions and creation of molecular electronic devices. Researchers from the Stanford University (USA) studied the adsorption of potassium atoms on semiconducting and *p*-type conducting NTs.[564] Theoreticians from the N S Kurnakov Institute of General and Inorganic Chemistry (Moscow, Russian Federation) calculated the properties of fluorinated NTs.[563] Their results are in agreement with those reported by Kelly *et al.*[104] who showed that fluorinated isomers capable of forming ring-like fluorinated sections should be the most stable.

Ouyang *et al.*[565] experimentally and theoretically studied the atomic structure and electronic properties of metal–semiconductor and metal–metal heterojunctions in SWNTs. This appeared

to be a step towards fabrication of intramolecular heterojunctions.

The first biological study of the structure of malaria-infected erythrocytes using an AFM with an NT probe tip was reported by Nagao *et al*.[566] The space resolution obtained using an NT probe tip was four times better than with the Si probe.

Mattson *et al*.[567] proposed the use of functionalised NTs as substrates for neural growth.

Nanotubes appeared to be excellent sorbents for purification of waste gases from low concentrations of highly stable carcinogenic dioxins.[568] In this respect, NTs are more efficient than activated carbon and sorbents based on porous graphite.

New procedures for preparation of NTs at moderate temperatures have been developed. One of them consists in reduction of hexachlorobenzene with potassium in the presence of bimetallic Co–Ni catalyst at 350 °C,[569] while the second involves hydrolysis of $Al(OBu^s)_3$ in the presence of acetylacetone or acetic acid and $Co(NO_3)_2 \cdot 6H_2O$, followed by gelation, drying of the gel and heating to 300–400 °C.[570]

A method for quantitative determination of the NT content in the reaction products using conjugated polymer filtration was first developed.[571] The method involves preparation of a NTs–polymer composite dispersion of the composite in toluene and storage until complete precipitation of impurities for at least 48 h.

A method for obtaining stable colloidal solutions of carboxylated SWNTs in water, ethanol, acetone and DMF was proposed[572] and some of their nonlinear optical properties were measured. These solutions were shown to be promising for the use in optical information processing systems.

The synthesis of NTs decorated with hydrated RuO_2 was reported.[573] Using these NTs, the specific capacity of electrochemical capacitors was enhanced up to 560 F g^{-1}.

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