

# Chemical modification of carbon nanotubes

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The current worldwide research on carbon nanotubes (CNTs) has been facilitated by unique physico-chemical properties and wide opportunities the CNTs offer for the new field of nanotechnology. The recent studies have shown that, for the efficient use of CNT structural properties, particularly in the engineering of multi-functional materials, the CNTs need to be chemically modified by attachment of functional groups for improving the solubility, processing and compatibility with host materials. While responding to the application needs, chemical modification of carbon nanotubes has quickly emerged as a new research frontier, which is fascinating from not only applied but also fundamental standpoint by permitting studies of chemical reactivity in relation to the nanoscale size and shape of confined structures.

Carbon nanotubes discovered by Iijima<sup>1</sup> are tubular nanocrystalline carbon clusters structurally built from rolled graphene sheets closed at the ends by the fullerene caps. Single-walled nanotubes (SWNTs) consist of a single graphitic cylinder, while double- and multi-walled nanotubes (DWNTs and MWNTs) are accordingly made of two or more concentric graphitic layers surrounding the central tubule.<sup>2–4</sup> Diameters of SWNTs and DWNTs can range from 0.4 to 4 nm and those of MWNTs, from 4 to 100 nm. Different synthesis and purification methods yield nanotubes that can be from 100 nm to several microns long. Carbon nanotubes possess unique mechanical properties, such as high stiffness, tensile strength and resilience, and depending on their diameter and helicity can be metallic, semi-conducting or insulating. This combination of remarkable properties makes them attractive candidates for a myriad of applications, e.g., design of lightweight superstrong polymer composites and fibers, nanoelectronic devices and sensors.<sup>4,5</sup> There is also a great interest in using the nanotubes for medical and biological applications.<sup>6,7</sup> This interest is prompted by the cylindrical surface morphology of the nanotubes, which are stable with respect to cage opening under *in vivo* environments.

Nanotubes tend to self-assemble into bundles in which up to several hundred tubes are held together by van der Waals forces. For many applications, the separation of individual nanotubes from their bundles is essential. To solve this problem, non-covalent<sup>8–11</sup> and covalent<sup>7,12–15</sup> modifications of nanotubes are

being pursued. Non-covalent modifications are based upon physisorption of molecules and polymers on CNT surfaces. The covalent modifications involve chemical functionalization by the attachment of various functional groups to the ends or sidewalls of the nanotubes through covalent bonds. Besides improving the solubility and processibility, the covalent modification also opens an opportunity for altering the structural and electronic properties of the nanotubes and obtaining new types of nanotube-based materials with useful properties. On contrary, the chemical functionalizations of the nanotube ends bring only a highly localized transformation of the nanotube electronic structure and do not change the bulk properties of these materials.

The challenges chemists face in the modifications of the SWNTs are related to poor reactivity of their sidewalls caused by high stability of graphene polyaromatic structure, much lower curvature of nanotube walls than in more reactive fullerenes,<sup>5</sup> and growing strain in the tubular frame with the number and size of functional groups attached to graphene walls. More challenges come with the necessity of nondestructive attachment of functional groups to the graphene walls in order to preserve the tubular structure. Therefore, appropriate choices of reagents and experimental conditions become decisive. The  $sp^2$ -bonding states of all carbon atoms, building the nanotube 'smooth' framework, facilitate the predominant occurrence of addition reactions. As the result, the hybridizations of the large part of carbon atoms transform into  $sp^3$  states that significantly



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alter the intrinsic properties of the nanotubes whose surface becomes ‘bumpy’ due to sidewall modification. The characterization of modified nanotubes presents additional challenge since spectroscopic methods routinely applied for analysis of small molecules are not adequate for high surface area nanosize carbon clusters for which materials characterization microscopy and surface analysis techniques have to be employed.

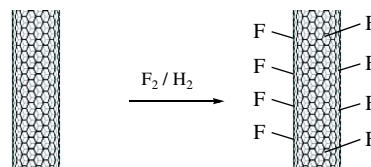
Carbon nanotubes in an ‘as produced’ form usually contain large quantities of residual metal catalysts. Purification processes involve oxidation; therefore, detailed studies of the stability and reactivity of CNTs towards different oxidants were carried out. It was shown that the caps on MWNTs can be open by oxidation with oxygen, air or carbon dioxide at temperatures above 700 °C. Oxidation in air or oxygen results in etching away of the tube caps and the thinning of tubes through layer-by-layer peeling of the outer layers, starting from cap regions. Carbon dioxide reacts as a milder oxidizing agent, which erodes and strips the cap of the tube exposing the terminated cylinder layers.<sup>16</sup> Heating MWNTs with Pb<sub>3</sub>O<sub>4</sub> in an inert atmosphere facilitated opening at a lower temperature (~400 °C).<sup>17</sup>

Treatments of SWNTs by sonication in HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> mixtures<sup>18,19</sup> were found to cut the nanotubes by oxidizing/etching action to lengths ranging from 100 nm to 1 micron and generate carboxyl groups and other oxo-functionalities predominantly on nanotube open ends, according to IR and <sup>13</sup>C NMR studies.<sup>20</sup> It was shown that in air the smaller diameter SWNTs are oxidized more rapidly than the larger diameter nanotubes.<sup>21,22</sup> The increased reactivity of smaller diameter SWNTs was also observed in experiments using room temperature oxidation by ozone.<sup>23</sup> The carboxylic acid groups (COOH), created at the open ends of the SWNTs, have been utilized in further chemical modifications by converting them into the corresponding acid chloride using SOCl<sub>2</sub>. Subsequent treatment of such obtained SWNT-COCl with NH<sub>2</sub>(CH<sub>2</sub>)<sub>11</sub>SH yielded an amide linkage of the nanotube end to the alkanethiol. The formation of a free thiol moiety has been verified by tethering the end of the nanotube to 10 nm diameter colloidal gold particles and imaging by AFM.<sup>18</sup> The alike thiol derivatized SWNTs have been assembled on gold substrates in orientation normal to the surface providing an ordered arrays of SWNTs useful for various applications, e.g., in field emission devices.<sup>24</sup>

The hydrogenated carbon nanotubes (H-CNTs) have been prepared from purified CNTs through a reduction process, utilizing Li and methanol in liquid ammonia.<sup>25</sup> The single-walled nanotubes, produced by laser ablation of graphite (L-SWNTs),<sup>23,31</sup> and MWNTs have been hydrogenated to approximately C<sub>11</sub>H composition determined from the yield of hydrogen evolved at elevated temperatures in the course of thermogravimetry–mass spectrometry (TG-MS) studies. Thus obtained H-NTs are thermally stable up to 400 °C. Above this temperature, the evolution of hydrogen and a small amount of methane takes place, peaking at 500 °C, which provide firm evidence for covalent C–H bonds present in these hydrogenated samples. Based on these experimental data, it has been suggested that the C–H bonds in H-NTs are weaker than those in aliphatic and aromatic hydrocarbons, but can be compared with the thermal stability of C–H bonds in hydroaromatic compounds. This is supported by the density functional theory (DFT) calculations data showing that the C–H bond energy in SWNTs, hydrogenated to their maximum capacity (~14 wt.%) for hydrogen storage, is substantially lower than in methane.<sup>26</sup>

The direct fluorination of the SWNTs with elementary fluorine results in the sidewall-fluorinated SWNTs (fluoronanotubes) (Scheme 1) representing a new family of nanoscale fluorocarbon materials. They were prepared by fluorination of both L-SWNTs<sup>19,27</sup> and nanotubes produced by a high-pressure disproportionation of CO (HiPco-SWNTs).<sup>28,29</sup> Extensive studies were carried out to establish optimal conditions (reaction temperatures, reaction times, addition of H<sub>2</sub> for *in situ* generation of HF catalyst) to reach a saturation stoichiometry (nearly C<sub>2</sub>F) without destruction of the tube structure.<sup>30</sup> With the participation of HF, which is a known catalyst for fluorination of

graphite, the saturated C/F ratio (~2) for the L-SWNT tube structure was reached at a lower reaction temperature (250 °C) than without HF. The other observed effect of HF was a noticeable upshift of the C–F stretching frequency in the ATR-FTIR spectra of fluoronanotubes, which indicated the formation of more covalent and, therefore, stronger C–F bonds. The same upshifting effect and a higher relative intensity of the C–F band in the IR spectra were also seen when raising the fluorination temperature. The SWNTs are essentially all destroyed when fluorinated at 400 °C and above to form a fluorographite. As a result of the side-wall functionalization of the SWNTs by fluorine, the electrical properties of the fluoronanotubes differ dramatically from those of pristine SWNTs. The fluoronanotubes prepared by fluorination at temperatures of 250 °C and above are insulators (two-point resistance across the length of buckypaper sample > 20 MΩ), while the pristine nanotubes are good conductors (two-point resistance 10–15 Ω).



**Scheme 1** Chemical modification of SWNTs by direct fluorination.

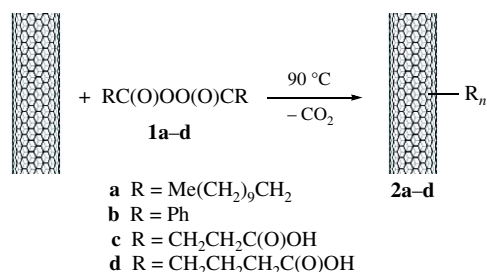
The HiPco-SWNTs have smaller average diameters (~1 nm) than L-SWNTs (~1.38 nm) and, therefore, are more reactive due to a higher curvature. This is particularly indicated by the observation that under the same fluorination conditions more fluorine can be attached onto the sidewalls of HiPco-SWNTs.<sup>13</sup> For instance, in the presence of *in situ* generated HF, the near C<sub>2</sub>F composition of the HiPco-SWNTs has been produced at a fluorination temperature as low as 150 °C, while under the same conditions the L-SWNTs yielded the fluoronanotubes with a significantly lower fluorine content (C/F ratio higher than 3). In comparison, the direct fluorination of DWNTs<sup>31</sup> at 200 °C and treatment of arc-produced MWNTs with a BrF<sub>3</sub>/Br<sub>2</sub> mixture at room temperature<sup>32</sup> resulted in addition of fluorine atoms only to the sidewalls of outer shells yielding products with the CF<sub>0.30</sub> and CF<sub>0.30</sub>Br<sub>0.02</sub> stoichiometries, respectively.

EELS calculations using density functional theory suggested the existence of ionic and covalent bonding of fluorine to carbon in the fluoronanotubes.<sup>33</sup> The fluoronanotubes form metastable solutions in DMF, THF, and alcohols after sonication. The transmission electron microscopy (TEM) studies show the unroping of fluoronanotubes to a ten times smaller diameter bundles as compared to pristine SWNTs. The solvation of individual fluoronanotubes was also observed by dispersing them on a mica substrate and examining with atomic force microscopy (AFM).<sup>34</sup> The solutions in alcohols were stable for a few days to over several weeks. Among the series of alcohols studied, 2-propanol and 2-butanol were found to be the best solvents. This solvation has been explained by hydrogen bonding between the hydroxyl hydrogen in alcohol and the nanotube-bound fluorine: R–O–H...F–(C<sub>n</sub>F). This bonding is likely facilitated by an increased ionic nature of the C–F bond in fluoronanotubes in contrast with alkyl fluorides, in which, according to recent studies, the fluorine is suggested to be a poor hydrogen bond acceptor.<sup>35</sup>

The imaging by scanning tunneling microscopy (STM) aided by the molecular modeling calculations provided insights into the possible fluoronanotube structures.<sup>36</sup> The STM imaging studies show the fluorinated regions to appear as bands around the circumference of the tube. Since the calculated at various levels of theory energy difference between the possible 1,2- and 1,4-isomers is small,<sup>36,37</sup> both types of fluorine addition can occur simultaneously during the fluorination process and form discrete isomeric domains on the nanotube.

Studies of thermal decomposition of C<sub>2</sub>F fluoronanotubes *in vacuo* at temperatures of up to 800 °C by VTP-MS indicated that the pyrolysis of fluoronanotubes is dominated by formation of volatile carbon-fluorine-containing molecules and not just the loss of elementary fluorine. These results and the observation of

the extended dark bands in the STM images of the partially fluorinated SWNTs  $C_nF$  ( $n > 2$ ) due to bare nanotube side walls have led to the idea of using fluorination followed by pyrolysis as chemical ‘scissors’ for cutting the nanotubes. Recently, this idea was implemented into a process in which the catalyst-free purified HiPco-SWNTs are first fluorinated to a stoichiometry of  $C_3F$  and thereafter heated at temperatures up to 1000 °C in an argon atmosphere to produce the nanotubes cut at the fluorinated sites to short lengths (20–200 nm).<sup>38,39</sup> When the pyrolysis process was monitored *in situ* with TGA-FTIR, the fluorine was shown to be driven from the fluoronanotube structure as  $CF_4$  and  $COF_2$  (due to oxygen covalently attached to the SWNT side-wall during the first steps of the purification procedure<sup>40</sup>). The AFM images have shown drastically shortened lengths in comparison with the pristine SWNTs. Note, that under the same conditions, the shortening of nanotubes does not take place when fluoronanotubes are mixed with a polyethylene matrix. In this case, TGA-FTIR studies show evolution of HF and lack of any volatile fluorocarbon molecules. The SEM images of TGA residues from fluoronanotube/polyethylene mixtures show mats of long nanotube ropes. This finding precipitated the idea of possible *in situ* covalent bonding of fluoronanotubes to a polyethylene matrix during melt processing, which explained the observed increase in mechanical properties of composites made.<sup>41</sup>



**Scheme 2** Chemical modification of SWNTs by reactions with organic acyl peroxides.

Carbon nanotubes, like their fullerene relatives, can also act as an organic free radical ‘sponge’. In recent studies,<sup>42,43</sup> HiPco-SWNTs have been reacted with a series of organic peroxides, such as lauroyl (**1a**), benzoyl (**1b**), succinyl (**1c**), and glutaryl (**1d**) peroxides (Scheme 2), commonly used as radical precursors in polymerization processes. It was shown that the SWNTs can successfully add to their side walls a carbon-centred organic radicals, thermally generated from acyl peroxides.

Covalent modification of SWNTs by this fairly simple approach using the low cost commercially available peroxides **1a–d** has been established by absorption UV-VIS-NIR and FTIR spectra, Raman spectroscopy, TEM imaging and also TG-MS and TG-FTIR analyses of weight loss and volatile products indicating that in derivatives **2a** and **2b** approximately 1 in 12 and 1 in 8 sidewall carbons, respectively, carry an attached group.<sup>42</sup>

This modification method has been further developed by adding the alkyl groups terminated with a carboxylic acid moiety to the nanotubes.<sup>43</sup> This method, which in comparison to hydroperoxide treatment is non-destructive to the sidewalls, utilizes the organic acyl peroxides of dicarboxylic acids **1c,d** as precursors for the corresponding ‘functional’ radicals. Succinic acid peroxide **1c** decomposes to form a  $HO(O)CCH_2CH_2COO\cdot$  radical, which can subsequently lose  $CO_2$  to yield a 2-carboxyethyl radical. Glutaric acid peroxide **1d** yields a 3-carboxypropyl radical *via* a similar route. These carboxyalkyl radicals react (Scheme 2) with the SWNTs to produce sidewall acid-functionalized SWNT-derivatives, ‘carboxyl’ nanotubes **2c** and **2d**, respectively. The attached carboxylic acid groups in **2c** and **2d** have been chemically characterized by formation of amide derivatives during subsequent reactions with thionyl chloride and several diamines, such as ethylenediamine, 4,4'-methylenebis(cyclohexylamine), and diethyltoluenediamine, and by instrumental methods: FTIR, Raman, UV-VIS-NIR, TG-MS, TEM and solid state  $^{13}C$  NMR.<sup>43</sup> The degree of SWNT

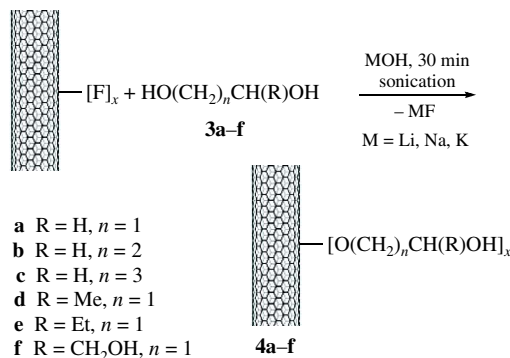
sidewall functionalization with the acid-terminated groups in **2c,d** was estimated as 1 in 24 carbons based on TG-MS data. The solubility data show that unlike the pristine nanotubes, the derivative **2c** is soluble in isopropanol and water ( $\sim 0.1$  g dm<sup>-3</sup>).

The DFT calculations of the electronic densities of states have shown that the Fermi energy of the fluoronanotubes is considerably shifted towards lower values compared to the pristine SWNTs. The conduction bands are energetically lowered as well.<sup>37</sup> This implies that the fluoronanotubes are better electron acceptors than the bare carbon nanotubes. Therefore, they should more eagerly interact with strong nucleophilic reagents, as well as undergo reduction to bare SWNTs by alkali metals. These chemical reactions are also facilitated by the fact that the C–F bonds in fluoronanotubes as in fluorinated fullerenes<sup>44</sup> are weakened relative to the C–F bonds in alkyl fluorides owing to an eclipsing strain effect,<sup>45</sup> and thus fluorine could be more easily displaced. The unique electronic structure, improved solubility of fluoronanotubes and the weaker C–F bond have opened new opportunities for chemical syntheses of a wide variety of sidewall functionalized nanotubes with interesting properties using fluoronanotubes as precursors.

Strong nucleophiles, such as alkyl lithium reagents, can be used to attach alkyl groups to the sidewalls of the nanotubes.<sup>13</sup> The reactions have been carried out by adding RLi ( $R = \text{methyl, } n\text{-butyl, } t\text{-butyl, } n\text{-hexyl and phenyl}$ ) reagents to the fluoronanotubes dispersed in THF, ether or hexane at  $-40$  °C followed by sonication for 10 min and stirring at room temperature overnight under argon. After completion of the workup procedure, the final R-SWNT products were dried in a vacuum oven and then characterized by ATR-FTIR, UV-VIS-NIR, TGA and TGA-FTIR techniques.

The solubility of fluoronanotubes in alcohols prompted their modification through reactions with alkoxides. For instance, the sonication of fluoronanotubes ( $\sim C_2F$ ) in a methanol solution of sodium methoxide for 2 h resulted in methoxylated tubes with the stoichiometry of  $C_{4.4}F(OMe)_{0.25}$  suggested from electron probe microanalysis (EPMA). The functionalizations of the fluorinated SWNTs by methoxy, ethoxy and isopropoxy groups were also done by sonication in LiOH solutions in methanol, ethanol and isopropanol, respectively.<sup>13</sup> Based on the established high reactivity of F-SWNTs towards alkoxides, a simple one-step chemical method for preparation of the SWNTs functionalized with the hydroxyl group terminated moieties (‘hydroxyl nanotubes’) has been developed. Such a method of attaching the functional groups through the sidewall C–O bonding (Scheme 3) involved reactions of F-SWNTs with a series of alkane diols and triols pre-treated with the alkali bases MOH.<sup>46</sup> The series included ethylene glycol **3a**, 1,3-propanediol **3b**, 1,4-butanediol **3c**, 1,2-propanediol **3d**, 1,2-butanediol **3e**, and glycerol **3f**. The alcohols, diols and glycerol, were used both as solvent media and as reagents to provide a surplus of hydroxyl-terminated monoalkoxides through the reactions with alkali base.

The synthesized ‘hydroxyl nanotubes’ **4a–f** were characterized by optical spectroscopy, ATR-FTIR, Raman, and UV-VIS-NIR, TEM, AFM, and thermal degradation – TGA and VTP-MS materials characterization methods. The characterization of ‘hydroxyl



**Scheme 3** Modification of fluoronanotubes *via* reactions with alkoxides derived from diols.

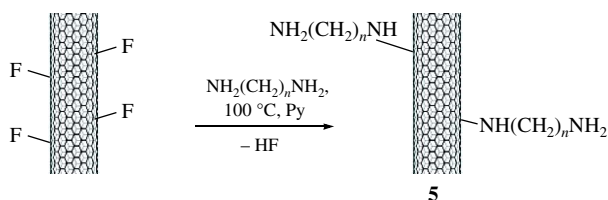


nanotube' derivatives by Raman spectroscopy has provided essential and quick information for evaluation of the covalent sidewall modification of the nanotubes. The Raman spectra collected for all of these SWNT derivatives display a peak in the region 1285–1300 cm<sup>-1</sup> related to the *sp*<sup>3</sup> states of carbon and serve as a sure proof of the disruption of the aromatic system of  $\pi$ -electrons on the nanotube sidewalls by the attached functional groups.

The EDX elemental analyses showed 3–5 at.% residual fluorine content in these derivatives. The degree of sidewall functionalization in **4a–f** was estimated to be in the range of 1 in 15 to 25 carbons, depending on alcohol reagent used. All prepared 'hydroxyl nanotube' SWNT derivatives have shown improved solubility in polar solvents as compared with pristine SWNTs. The solutions of glycerol-SWNT derivative **4f** in water (~40 mg dm<sup>-3</sup>) were stable for several days, while ethanol solutions with higher **4f** concentration (~80 mg dm<sup>-3</sup>) showed some precipitation only after several months.<sup>46</sup> The applications of so prepared SWNT derivatives will be based on hydrogen bonding ability and chemical reactivity of terminal hydroxyl groups in the side chain.

The amino group terminated SWNT derivatives, 'amino nanotubes', have been prepared by interactions of fluoronanotubes with the terminal diamines, H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> (*n* = 2–4, 6).<sup>47,48</sup> The reactions (Scheme 4) were carried out by refluxing the F-SWNTs in the corresponding diamine for 3 h in the presence of catalytic amounts of pyridine (Py). The EDX analyses of black precipitates yielded a nitrogen content within 11–16 at.%, and a very low (1–2 at.%) fluorine content, suggesting its efficient displacement by the N-alkylamino functionalities. All prepared amino-SWNT derivatives **5** have been tested positively by Kaiser testing procedure for the free NH<sub>2</sub> groups. The TGA-FTIR, Raman and VTP-EIMS studies provided strong evidences for covalent functionalization, showing a major loss of the attached groups at ~325 °C and restoration of the original *sp*<sup>2</sup>-bonded carbon framework.<sup>47,48</sup>

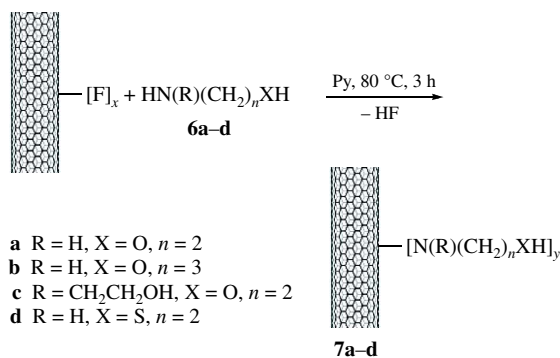
Unlike these reactions, treatment of F-SWNTs with the simplest diamine, hydrazine H<sub>2</sub>NNH<sub>2</sub> resulted in their complete defluorination *via* the following reaction: 4C<sub>n</sub>F (F-SWNT) + N<sub>2</sub>H<sub>4</sub> → 4C<sub>n</sub> (SWNT) + 4HF + N<sub>2</sub>.<sup>13</sup> This reaction provides a useful tool for chemical modification of the side walls of the SWNTs, which can be applied for controlled partial defluorination of fluoronanotubes to produce SWNTs with varying fluorine contents and, presumably, different properties.



**Scheme 4** Modification of fluoronanotubes by reactions with diamines.

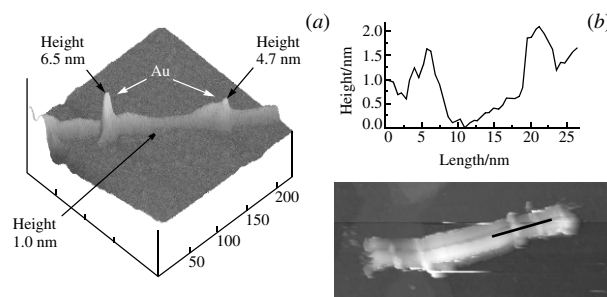
Since diamines can react with fluoronanotubes by sidewall C–N bond forming interaction, the simplest diamide, such as urea,<sup>49</sup> amino acids,<sup>7,14</sup> amino alcohols<sup>46</sup> and 2-aminoethanethiol<sup>50</sup> were also chosen to react with the fluoronanotubes in the presence of pyridine through their NH<sub>2</sub> end groups. By this way, the method of F-SWNTs sidewall C–N modification has been extended to the other amino group-terminated reagents. For instance, the reactions of fluoronanotubes with amino alcohols (Scheme 5), such as 2-aminoethanol **6a**, 3-aminopropanol **6b**, diethanolamine **6c**, and 2-aminoethanethiol **6d** in the presence of pyridine as a catalyst consequently yield the hydroxyl group-terminated SWNT derivatives **7a–c**, thus providing another method for synthesis of 'hydroxyl nanotubes'.<sup>46</sup>

In the case of derivative **7d**, in addition to characterization by Raman, ATR-FTIR and TGA methods, the presence of terminal thiol groups on SWNT sidewalls was established by using the ability of sulfur to form a strong coordination bond with gold. For this purpose, the thiol functional groups in **7d** were 'tagged' with 5 nm size gold nanoparticles. The AFM imaging and



**Scheme 5** Modification of fluoronanotubes by reactions with amino alcohols or thiols.

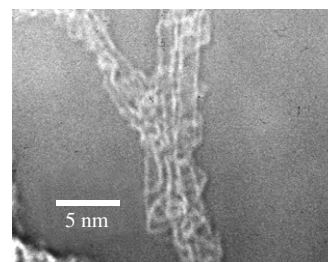
height measurements of the single gold 'tagged' **7d** nanotube [Figure 1(a)] clearly showed the presence of individual gold nanoparticles decorating the side of the nanotube. Direct imaging of the substituents on **7d** was performed by STM analysis after placing the sample onto Au(111) surface. High resolution STM images of **7d** [Figure 1(b)] show that multiple functional groups are present on the nanotube in tight bands of approximately 5–25 nm in length.<sup>50</sup>



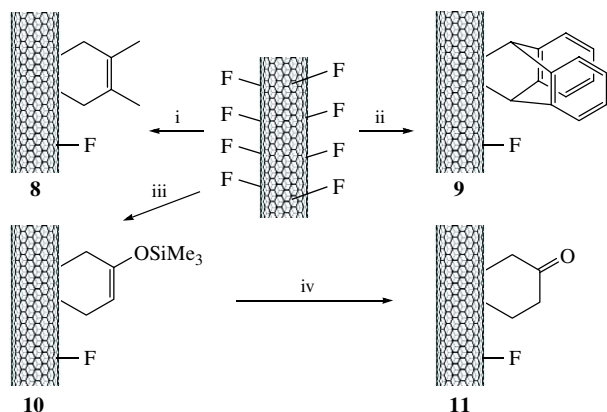
**Figure 1** High resolution microscopy images of thiol-modified SWNTs **7d**: (a) 3-dimensional AFM image of gold 'tagged' **7d**; (b) STM image of a **7d** placed on gold surface. Rings show the distribution of thiol terminated functional groups along the backbone of nanotube. The graph above the image shows the height and length of the bands formed by functional groups attached to the chosen section of nanotube.

The fluoronanotubes have also been reacted with lauroyl and benzoyl peroxides under the same conditions as pristine SWNTs in order to compare the reactivity of their corresponding polyaromatic and conjugated polyene  $\pi$ -systems toward radical addition. Both reactions resulted in successful attachment of undecyl and phenyl radicals to the sidewalls of fluoronanotubes along with the substantial removal of fluorine. The addition of undecyl radicals, C<sub>11</sub>H<sub>23</sub>, generated from lauroyl peroxide, was proceeding more readily than in case of pristine SWNTs, as indicated by a much lower reaction time (3 h vs. 5 days).<sup>42</sup> The covalent attachment of long-chain groups to the side walls in these modified nanotubes was imaged by TEM (Figure 2) and confirmed by TGA-FTIR and VTP-MS data, indicating the major loss of undecyl radicals and their dimer at 350–400 °C.

Since in the fluorinated SWNTs a large fraction of the sidewall carbons becomes tetrahedral, the bond strain of the residual

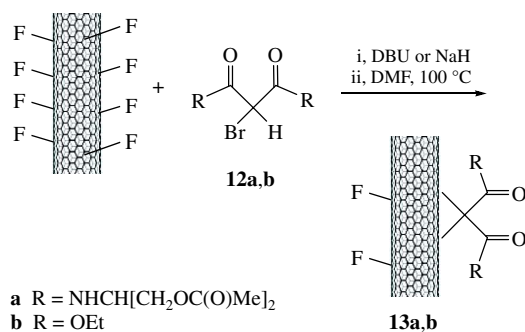


**Figure 2** High-resolution TEM image of fluoronanotubes modified by reaction with lauroyl peroxide. Long-chain undecyl moieties attached to the sidewalls of nanotubes are clearly seen.



**Scheme 6** Modification of fluoronanotubes by Diels–Alder cycloaddition reactions: (i) 2,3-dimethyl-1,3-butadiene; (ii) anthracene; (iii) 2-trimethylsiloxy-1,3-butadiene; (iv) atmospheric  $\text{H}_2\text{O}$ .

olefinic moieties is increased as compared to aromatic in pristine SWNTs. In addition, the presence of electron withdrawing substituents further enhances the rate of addition of electron-rich molecules. Thus, the fluoronanotubes may be considered as a source of ‘activated’  $\text{C}=\text{C}$  bonds on the SWNT sidewall. Besides the earlier demonstrated free radical additions,<sup>42</sup> this concept has also been verified by studies of the [4+2] Diels–Alder cycloaddition<sup>51</sup> and addition of carbene through Bingel-type reaction.<sup>52</sup> The fluoronanotubes were shown to undergo a facile reaction with a series of dienes (Scheme 6) that resulted in modified SWNTs with the degree of carbon to substituent ratio from 20/1 to 32/1. The IR, Raman, AFM and  $^{13}\text{C}$  NMR characterizations<sup>51</sup> are consistent with sidewall functionalization proceeding more efficiently and under milder conditions than in case of pristine SWNTs. The reactions of fluoronanotubes with bromomalonate reagents **12a,b** (Scheme 7)<sup>52</sup> in the presence of a strong base resulted in SWNT derivatives **13a,b**, while pristine SWNTs remained almost intact under the same reaction conditions. Covalent sidewall attachment in **13a,b** was verified by ATR-FTIR, Raman, VTP-MS and XPS data.



**Scheme 7** Modification of fluoronanotubes via Bingel-type reactions with bromomalonate reagents.

In summary, the chemical modification of carbon nanotubes has become a new important research field with high expectations for future growth. The already developed chemical modification methods include oxidation, hydrogenation, fluorination, addition of free radicals and other reactive molecules. Collaborative work with the N. D. Zelinsky Institute of Organic Chemistry and L. F. Vereshchagin Institute for High Pressure Physics of the Russian Academy of Sciences is in progress to also explore the carbene chemistry methods and high pressure techniques. Fluorine and other functional groups on the side walls of SWNTs surface significantly alter their physical properties (conductivity, solubility, etc.) and dramatically enhance their chemical reactivity. Therefore, oxidized nanotubes, as well as fluoronanotubes, are widely used as precursors for subsequent modifications. The functional groups chemically attached to the nanotubes assist effectively in unroping the nanotube bundles and dispersion in polymers and ceramics, crucial for nanocomposites fabrication.

The ‘tailored’ chemical modifications provide multiple sites for covalent bonding of nanotubes to polymer matrices for enhancement of mechanical properties, which were successfully demonstrated for epoxy,<sup>53,54</sup> vinyl ester,<sup>55,56</sup> polyethylene,<sup>41,57</sup> and polypropylene<sup>58</sup> composites filled with modified SWNTs. The fluorine modified SWNTs possess an ultra-low friction coefficients (0.002–0.07), making them attractive candidates for solid lubricant applications.<sup>59</sup> The SWNTs, surface functionalized with organic moieties, were shown to present a clear advantage in applications as ‘nanomatrices’ for MALDI mass spectrometry analysis of lipids, peptides and tissue samples due to large surface area absorbing biomolecules, wide optical absorption spectrum and extremely high analyte ionization efficiency.<sup>60</sup> Just these very few examples give a reason to believe that a variety of novel applications of chemically modified carbon nanotubes in nanocomposites, nanoelectronic devices, nanoengineered drug delivery systems, nanolubricants, etc., will continue to emerge from chemical research in the interdisciplinary field of nanotechnology.

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