Fullerene Pipes, Tube-in-Tube Membranes, and Carbon-Nanotube Tips: Adding New Dimensions to Molecular Technology

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Following the bonanza of fullerenes and endohedral metallofullerenes, other novel forms of carbon continue to spark great interest among chemists and physicists alike. These new varieties include single-wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs) as well as bucky onions. Several large-scale routes that lead to carbon nanotubes (NTs) are now available.[1] This article is intended to highlight recent advances in molecular technology involving carbon nanotubes.

In the focus of current interest are single-wall carbon nanotubes of molecular perfection ("fullerene nanotubes") as a result of their unique electronic and mechanical properties in combination with chemical stability.[2] Promising applications of SWNTs include, for example, the storage of hydrogen and other gases,[3] quantum wires,[4] electronic devices,[5] and catalyst supports.[6] Until now there was a striking paucity of fullerene structures in the intermediate size range between typical fullerenes and long SWNTs, namely with a length of 10 to 300 nm. These would be of paramount importance as possible connectors and components for molecular electronic devices. A recent publication by Smalley et al. makes such "fullerene pipes" readily available for the first time and opens up a highly promising new branch of molecular technology.[7]

The procedure that leads to fullerene pipes comprises several innovative steps. Crude SWNTs can be produced in a laser-oven in amounts of up to 20 g in two days by the use of a metal catalyst (Ni, Co, Fe).[1c,d] However, this scaled-up method yields a material that contains substantial amounts of nanoscale impurities (for example, amorphous carbon, bucky onions, and spheroidal fullerenes; Figure 1a). Thus an important first step is the purification of this SWNT material before cutting. It was found that refluxing the nanotubes in 2.6 M nitric acid and resuspending them in water with surfactant at pH 10 followed by filtration with a cross-flow filtration system afforded purified fullerene fibers in 10–20% yield (by weight). A crude material of particularly low quality was chosen to demonstrate the efficiency of the purification procedure. According to scanning electron microscope (SEM) and transmission electron microscope (TEM) imaging the fullerene fibers form endless ropes that are highly tangled with one another. A unique free-standing mat of these tangled SWNT ropes ("bucky paper", Figure 1b) could be made by passing a purified SWNT suspension through a polytetrafluoroethylene filter. Figure 1c shows a torn edge of this bucky paper. It is clearly seen that tearing results in substantial alignment of the fullerene ropes.

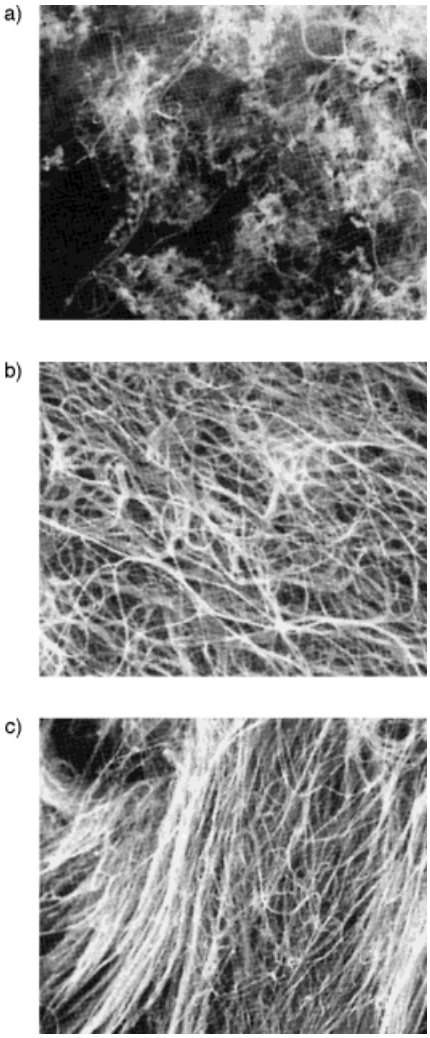

Figure 1. SEM images of a) raw SWNT material, b) purified bucky paper, and c) a torn edge of purified bucky paper (reprinted with permission from *Science*[7]).

The following step, namely, the cutting of the nearly endless, tangled ropes can be performed either by simply cutting the bucky paper with a pair of scissors or by more sophisticated techniques such as bombardment with relativistic gold ions. However, the best and most effective method was found to be ultrasonication of purified SWNT ropes in a 3:1 mixture of concentrated H_2SO_4:HNO_3 at 40 °C (Houston room temperature). The effect of this particular treatment is twofold: First, ultrasonication creates open holes in the tube side. Subsequent attack of the oxidizing acid mixture then occurs at the points of damage, which leads to the efficient cutting of the SWNT ropes into thinned rope pieces and individual cut tubes (Figure 2).

It was found that stable colloidal suspensions of the resulting "fullerene pipes" could be obtained in the presence

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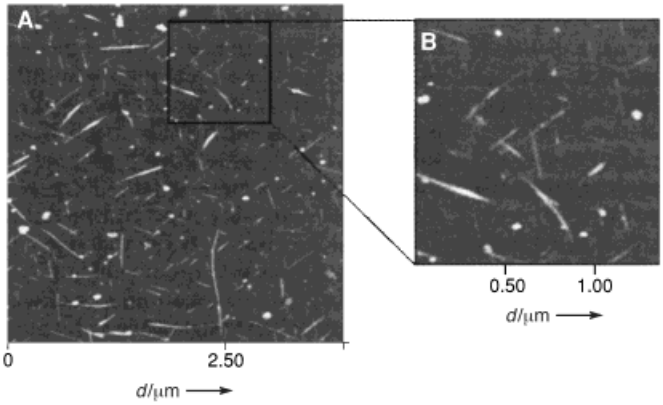

Figure 2. AFM images of fullerene pipes electrodeposited from a stable colloidal suspension onto HOPG (reprinted with permission from *Science*[7]).

of anionic or nonionic surfactants. Imaging of the cut tubes was effected by a newly developed electrodeposition technique in which all suspended nanotubes are deposited onto the surface of highly oriented pyrolytic graphite (HOPG). Scanning the sample by atomic force microscopy (AFM) revealed the effective cutting of the original endless ropes into fullerene pipes (Figure 2). It is noteworthy that the cut tubes show a tendency to align 120° to one another. This phenomenon, which is observed only for chemically clean and molecularly perfect fullerene tubes, reflects the molecular geometry of the underlying graphite lattice. In subsequent experiments it was demonstrated that it is possible to "polish" the cut tubes and further manipulate their average length. This was achieved by further etching the cut nanotube pieces in acid without ultrasound treatment. Mixtures of concentrated sulfuric acid and either nitric acid or H_2O_2 were employed successfully to systematically shorten the length distribution of the tubes, with the amount of shortening being dependent on the exposure time to the acid. Shortening rates between roughly 130 and 200 nm h^{-1} were realized and varied with the reaction conditions. Whereas it was found that the fullerene pipes flocculate rapidly in pure water, their colloidal suspensions prepared with the aid of surfactants are easy to handle and even allow a separation by length. Figure 3 shows different fractions of cut fullerene nanotube pipes as obtained by field-flow fractionation and analyzed by AFM imaging.

In this context a recent publication by Duesberg et al. should be mentioned, which reports the successful separation of multiwall carbon nanotubes (MWNTs) by size-exclusion chromatography (SEC).[8] Purified MWNTs of well-defined size distribution are of great potential interest for proposed applications such as field emission and electronic devices.[5, 9] In this case the major goal was the development of a nondestructive method for purification and size separation. Previously reported methods include destructive methods such as oxidation of the crude nanotube material. These methods are effective in decomposing small impurity particles, but they have certain disadvantages in that a significant amount of material is lost and no size separation can be achieved.[10] The main problem encountered with known nondestructive methods such as filtering is that the pores of the filters are easily blocked.[11] It has now been discovered

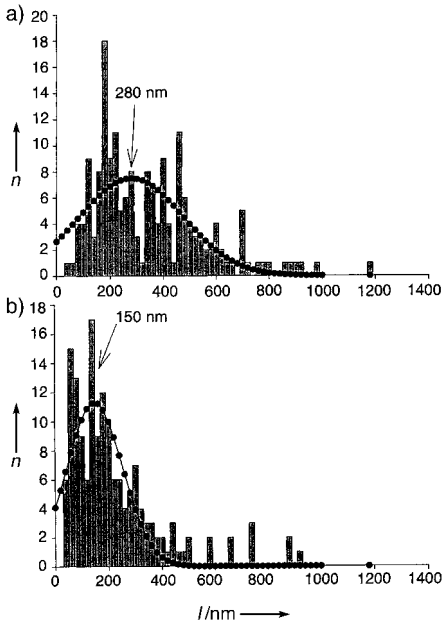

Figure 3. Histograms of cut nanotubes before (a) and after (b) stirring in a mixture of sulfuric and nitric acid (3:1) at 70 °C for 1 h (reprinted with permission from *Science*[7]).

that size-exclusion chromatography of crude nanotube material offers a highly efficient route to purified, chemically unmodified and size-separated MWNTs. SEC is known to be an excellent method for purifying, for example, biological macromolecules or virus particles. Fractionation of the MWNTs was achieved through the use of two successive columns packed with controlled pore glass (CPG) that had an average pore size of 140 and 300 nm, respectively. The CPG material used in this study is chemically inert and has the advantage of a narrow distribution of pore sizes. Characterization of the fractions was achieved by TEM and SEM imaging as well as through atomic force microscopy (AFM). Figure 4 demonstrates the absence of small spherical particles and hence the successful purification of the NTs. In addition, the method proved to be highly useful in achieving a separation of the nanotubes by size. A statistical evaluation of the size distribution in various fractions was carried out by SEM and AFM imaging of the samples after adsorption onto chemically modified Si wafers. As a result, the average MWNT length in different fractions of individual nanotubes varied between about 0.4 and 1 μm. It was pointed out that the method can easily be scaled up and could even be further improved by using HPLC techniques.

More recently, Duesberg et al. have been able to demonstrate that the SEC purification method is also applicable to SWNTs.[12] In this case oxidative methods cannot be applied because of the single-layer structure of the nanotubes, and known nondestructive methods such as filtration and/or flocculation are cumbersome as several filtration steps are necessary to achieve a reasonable purity. Once again SEC proved to be the method of choice for obtaining pure, chemically unmodified SWNTs and moreover allows some degree of size separation. The case of SWNTs is somewhat more complicated compared to the purification of multiwall nanotubes, because of the highly tangled nature of the nearly

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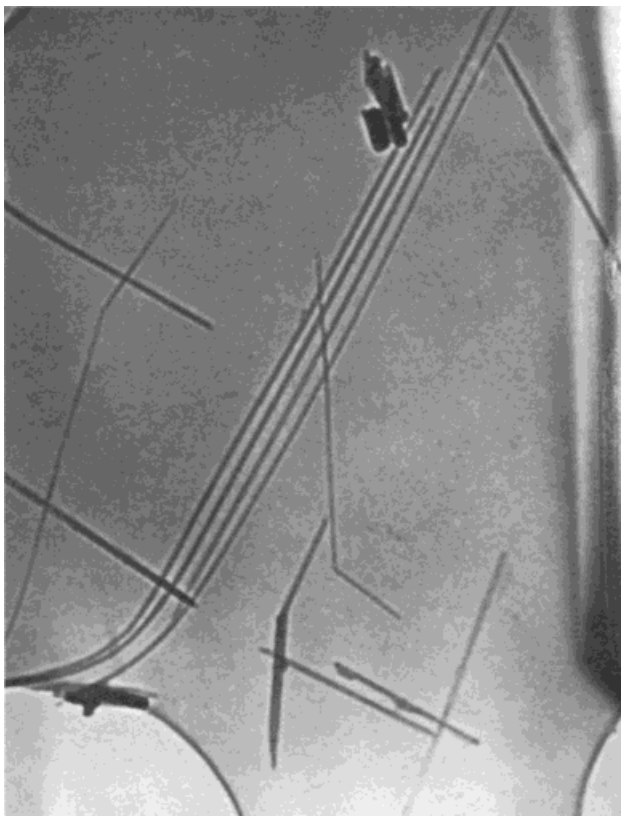

Figure 4. SEM image of purified MWNTs adsorbed on a chemically modified Si wafer (reprinted with permission from *Chem. Commun.*[8]).

endless ropes and as a result of extensive crosslinking by catalyst particles that are encapsulated by a shell of amorphous carbon. Purification by SEC was achieved by the use of surfactant-stabilized nanotube dispersions made with the assistance of ultrasonication. The dispersed nanotube material was found to move completely (except for a few larger network particles) through a column of controlled pore glass with an average pore size of 300 nm. Characterization of individual fractions by AFM and TEM was carried out as described above. These investigations revealed that fractions containing almost exclusively SWNTs could be obtained and that the average nanotube lengths differed significantly between various fractions.

Coming back to the fullerene pipes, yet another interesting aspect of the work by Smalley et al. is the chemical derivatization of these cut tubes at their open ends.[7] This experiment can be seen as an important first step in the direction towards the construction of molecular devices from fullerene tube assemblies. Following the assumption that the acid treatment leaves many carboxylic acid end groups at the open ends of the tubes, the fullerene pipes were treated with thionyl chloride to convert the end groups to the corresponding acid chloride functions. Further treatment with $H_2N(CH_2)_{11}SH$ in toluene afforded nanotubes with amide-linked alkanethiol end groups. The thiol end groups then allowed the functionalized tubes to be tethered to 10-nm gold particles. Figure 5 shows how most of the thiol-derivatized nanotubes have a single gold particle attached to one or both ends. In a control experiment it was verified that the

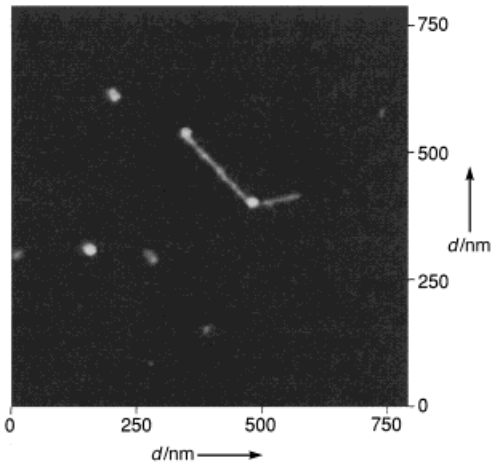

Figure 5. "Seven minutes to three": AFM image of two derivatized fullerene pipes tethered to a 10 nm diameter gold sphere. The longer pipe (the minute hand) has another gold particle tethered to its other end (reprinted with permission from *Science*[7]).

derivatization of the tube ends is a prerequisite for the cut SWNTs to be tethered to gold particles.

Arrays of functionalized fullerene pipes and metal particles are anticipated to be an important step towards the construction of molecular devices. The work by Smalley et al. also implies additional future applications with respect to a new area of molecular technology. For example, it was pointed out that the most interesting species, namely, small nanotubes shorter than 100 nm are lost during the newly developed filtration procedures. These would be of enormous interest as they approach the chemistry of molecular fullerenes. Future work in this field will undoubtedly be directed towards the isolation of such SWNTs with lengths less than 100 nm. Yet another exciting future option would be to close the open fullerene pipes at their open ends. This might simply be achieved by annealing at temperatures around 1000 – 1200 °C. The closing process should be guided by the same mechanisms as those that lead to the formation of fullerenes. According to Smalley, purified nanotubes will play an important role in the development of molecular electronics.[13] Each tube behaves as a coherent quantum conductor, and it is not beyond the imagination that "buckycables" will eventually be constructed from new carbon polymers. A most recent paper by Dai et al. shows that innovative experimentation even leads to significant improvements in the preparation of individual SWNTs.[13b] In a first step regularly patterned micrometer-scale catalytic islands were deposited on a Si wafer by covering the silicon surface with a polymethylmethacrylate (PMMA) film and creating square holes by electron beam lithography. The holes were then filled with a mixture of catalyst precursors ($Fe(NO_3)_3 \cdot 9H_2O$, $[MoO_2(acac)_2]$, Al_2O_3) followed by removal of the PMMA mask and heating the substrate to 1000 °C under an argon atmosphere. Chemical vapor deposition of methane on the catalyst-patterned substrate causes perfect, individual SWNTs with diameters of 0.8 to 3.0 nm and lengths of up to 20 μm to grow from the catalytic islands. Some SWNTs even bridge adjacent islands and thus create a macroscopic electrical network. These results will certainly have great impact on further research with individ-

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ual SWNTs, as the nanotubes made by the new technique are easily located, manipulated, and characterized by SEM and AFM imaging.

Another promising way of manipulating carbon nanotubes is their alignment under formation of membranes,[14] which was recently achieved by Martin et al.[15a] These researchers used a chemical-vapor deposition (CVD) approach with ethylene as a precursor (no catalyst is required). When the CVD process is carried out within the pores (200 nm diameter) of a commercially available alumina template membrane, a carbon nanotube is formed within each pore in addition to a 20-nm thick carbon surface film covering both faces of the template. The underlying alumina template can then be dissolved away in 46% HF solution to leave a free-standing carbon nanotube membrane. The surface film appears to have an important function as it holds the tubes together in the aligned fashion after removal of the alumina template. Figure 6 shows that the carbon tubes that make up these membranes are vertically aligned, and that the ends of these nanotubes are open.

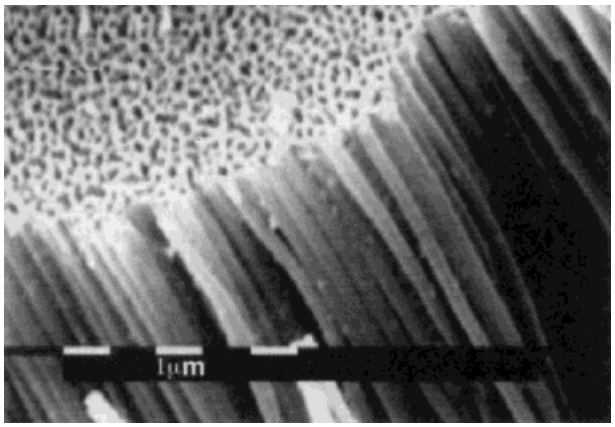

Figure 6. SEM image of a template-synthesized carbon nanotube membrane after dissolving the alumina template (reprinted with permission from *Nature*[15a]).

In an extension of this work catalytic nanoparticles were prepared within the CVD template-synthesized carbon tubes. This was accomplished by immersing the carbon/alumina membrane in aqueous solutions containing the desired metal ions such as H_2PtCl_6, $H_2PtCl_6/RuCl_3$, or $Fe(NO_3)_3$. After immersion, the membranes were dried in air, and the metal ions were reduced to the corresponding metal or alloy in a hydrogen stream at 580°C. Dissolution of the alumina template was carried out as described above for the metal-free membranes. Figure 7 depicts a TEM image of a single tube that was removed from a membrane by ultrasonication, and in which the Pt/Ru nanoparticles can be clearly seen through the tube walls. It was demonstrated that such catalyst-loaded membranes can be employed to electrocatalyze O_2 reduction and methanol oxidation. Both reactions are of importance to fuel-cell technology.

It was further found that iron nanoparticles deposited inside the tubes can be used as catalysts for the CVD growth of narrower nanotubes within the template-synthesized tubes ("tube-in-tube membranes").[15a] Figure 8 shows such a Fe-catalyzed CVD inner nanotube inside an outer tube. These

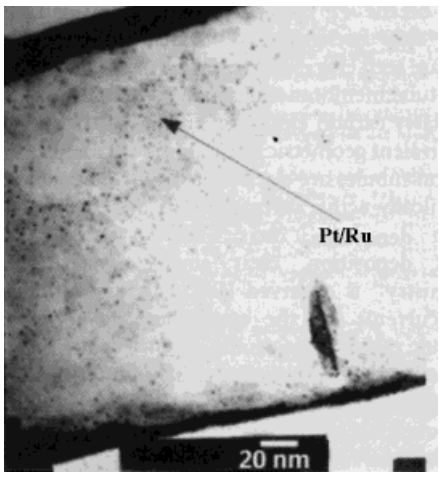

Figure 7. TEM micrograph of a tube filled with Pt/Ru nanoparticles (reprinted with permission from *Nature*[15a]).

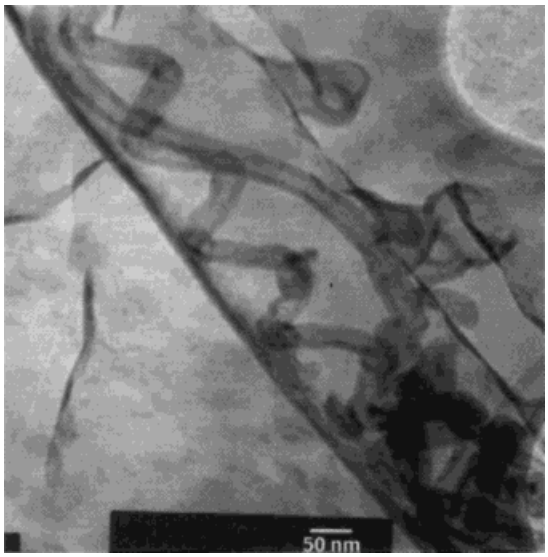

Figure 8. TEM micrograph of the inner carbon nanotubes prepared by Fe-catalyzed CVD inside the outer template-synthesized tubes (tube-in-tube membranes) (reprinted with permission from *Nature*[15a]).

findings are expected to have an impact on the improvement of lithium-ion batteries as carbon is the anode material of choice in such batteries. It was indeed found that the nanotube membranes reversibly intercalate Li^+ ions. Moreover, the intercalation capacity was more than doubled when the tube-in-tube membranes were used. This is the first case where reversible lithium ion intercalation has been demonstrated for carbon nanotubes.

Carbon nanotubes are also known to be very good electron emitters. This is why since their discovery there has been a lot of speculation about the use of nanotubes in the construction of flat-panel devices. However, a prerequisite for a major break-through in this area would be their perfect alignement on a flat surface. Recently Ren and co-workers succeeded in growing large arrays of well-aligned carbon nanotubes on nickel-coated glass.[15b] Their method involved plasma-enhanced chemical-vapor deposition using acetylene gas as the carbon source and ammonia gas both as catalyst and dilution gas. The use of ammonia allowed the reaction to proceed at

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temperatures below 666 °C, which corresponds to the strain point of the best display glass. After removal from the underlying glass carrier SEM imaging showed that the nanotubes were uniformly aligned across the whole surface and each was capped with nickel. It was found that the diameters of the nanotubes, which varied from 20 to 400 nm, was controllable by changing the thickness of the nickel layer. These results can be considered a good step toward the construction of flat-panel displays with carbon nanotubes.

Yet another exciting field of innovative application for carbon nanotubes has recently been explored by Lieber et al. These researchers have investigated the use of carbon-nanotube tips and functionalized nanotubes as high-resolution probes in chemistry and biology. Based on findings by Smalley et al.[16] their first paper reports an atomic force microscopy (AFM) imaging study with carbon-nanotube tips.[17] The resolution of AFM is generally limited by the size and shape of the commercially available pyramid-shaped silicon probe tips. A significant improvement has now been achieved by attaching MWNTs or SWNTs to the ends of single-crystal silicon cantilever tip assemblies (Figure 9). Technically this can be achieved under the direct view of an optical microscope using an acrylic adhesive.

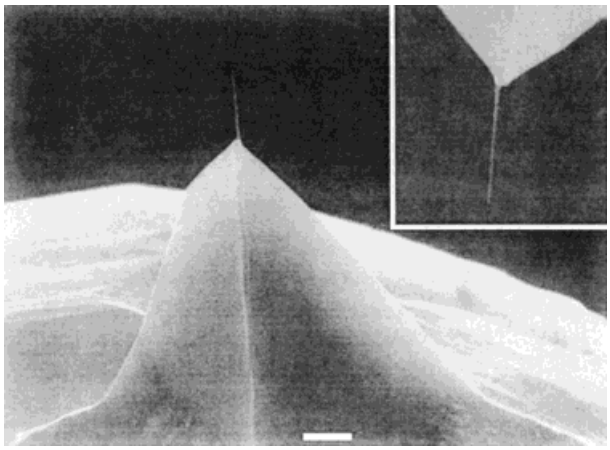

Figure 9. SEM image of a MWNT tip attached to a silicon cantilever tip assembly. The white bar corresponds to 1 μm (reprinted with permission from *J. Am. Chem. Soc.*[17]).

Imaging by AFM revealed that the major portion of the nanotube tip corresponds to bundles of tightly packed tubes. The average MWNT tips exhibited radii of 9 nm as compared to 13–20 nm for Si probe tips. As a further advantage it was found that in the case of contamination or other deterioration the nanotube tips could be easily shortened and regenerated by a simple field evaporation technique. In AFM studies the MWNT tip assemblies have been demonstrated to exhibit a superior performance with respect to probing deep crevices and steep features (for example, in microelectronic devices) as well as delicate organic and biological samples. No damage of such biological objects is encountered as the nanotubes have been shown to buckle elastically above a critical force.[18] The efficiency of carbon nanotube tips in the high-resolution imaging of biological samples was tested by investigating Aβ40 fibrils, which play a role in Alzheimer's disease.[19] Such Aβ fibrils had been investigated previously by atomic force microscopy.[20] Figure 10 shows a typical image of an Aβ fibril obtained by the MWNT tip technique. This image features a significantly higher resolution than previous AFM studies and even shows a detail not revealed by other methods, namely the decrease in size after the branching point. Further

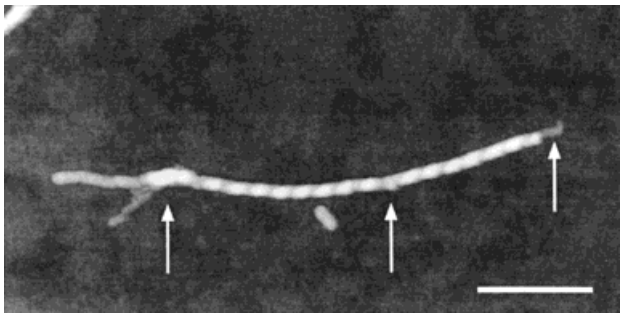

Figure 10. Typical AFM image of a Aβ40 fibril acquired with a MWNT tip. The white bar corresponds to 250 nm (reprinted with permission from *J. Am. Chem. Soc.*[17]).

improvements of the newly developed method are expected from the use of SWNT tips that have average radii of only 3 nm. Even true molecular resolution could eventually be approached when it becomes possible to expose individual nanotubes at the tip ends. Individual SWNTs have radii on the order of only 0.5 nm.[21b]

Potential applications in various areas of chemistry and biology can be expected from molecular probes based on covalently functionalized nanotubes, which have also been described recently by Lieber et al.[21] This work addresses the question as to whether carbon nanotubes could be chemically modified in such a way that they would sense and manipulate matter at the molecular level. The general approach is related to the functionalization of fullerene pipes as reported by Smalley et al.[7] and makes use of the fact that oxidized nanotubes are terminated at their open ends by carboxyl groups. It was found that these carboxyl end groups can be "titrated" using the method of chemical force microscopy (CFM), that is, by measuring the adhesion force between the MWNT tips and a self-assembled monolayer (SAM) substrate terminating in hydroxyl groups (for example, 11-thioundecanol on gold-coated mica) at different pH values.[21a] Such force titrations revealed a well-defined drop in the adhesion force around pH 4.5, which corresponds to the deprotonation of the carboxylic end groups. Chemical modification of the tube ends was achieved by coupling the carboxyl groups with either benzylamine or ethylenediamine in the presence of a suitable water-soluble carbodiimide (Figure 11). These experiments unambiguously verify the presence of carboxyl groups exposed at the ends of nanotube tips and provide probes modified with either non-ionizable hydrophobic (benzylamine) or ionizable (ethylenediamine) end groups.

It was then assumed that there should be significant differences in the adhesion force between, for example, the carboxyl-terminated nanotube tips and either COOH-terminated SAMs or CH_3-terminated SAMs.[21a] Vice versa, the tips covalently modified with benzylamine should interact more strongly with the CH_3 than with the COOH regions of a SAM substrate. Indeed, using the functionalized nanotube probes it

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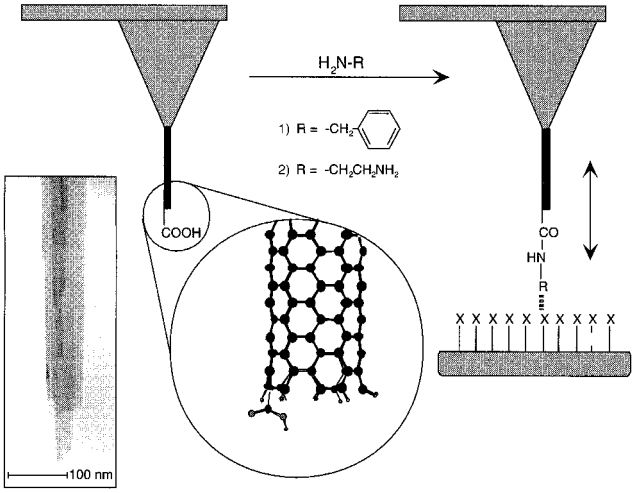


Figure 11. Diagram illustrating the chemical modification of a carboxyl-terminated nanotube tip by coupling with an amine, and the application of this probe to chemically sensitive imaging (X = functional groups of a substrate surface). The MWNT tips are attached to the pyramids of gold-coated Si cantilevers (reprinted with permission from *Nature*[21a]).

was possible to visualize patterned substrates. Figure 12 shows the functionalized nanotube mapping of a substrate patterned with squares terminating in CH_3 groups and surrounded by areas terminated by COOH groups. The observed differences in phase between the two sample areas are a result of phase-lag differences, which can be related to differences in the adhesion forces. In other words, the method can be used to visualize differences in the chemical functionality even though there is no difference in height between the substrate areas.

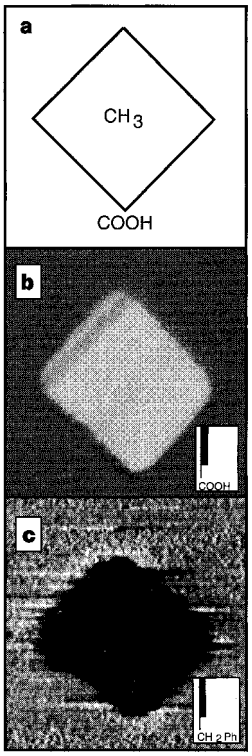
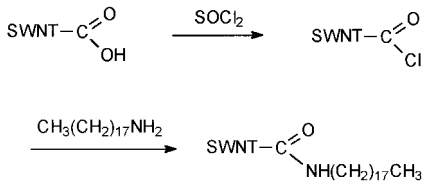


Figure 12. Chemically sensitive imaging of patterned substrates using functionalized nanotube tips. a) Schematic diagram of a patterned sample consisting of methyl-terminated squares surrounded by a COOH-terminated area; b) image of the patterned sample recorded with an unmodified (COOH-terminated) nanotube tip, and c) image recorded using a benzylamine-modified (phenyl-terminated) nanotube tip (reprinted with permission from *Nature*[21a]).

Most recently the modification strategy has been successfully extended to SWNTs.[21b] Selectively modified SWNT tips have been shown to produce images of chemically patterned sample with extraordinarily high lateral resolution. The chemical modification of the end groups has also been used to solubilize SWNTs for the first time in common organic solvents.[22] Purified SWNTs were obtained following Smalley's procedure[7] and converted into the COCl derivatives by treatment with thionylchloride. The key to the successful preparation of soluble SWNTs (*s*-SWNTs) was the reaction of SWNT-COCl with excess octadecylamine at elevated temperatures [Equation (1)]. During this process the volume of the



(1)

nanotubes increases several times, which indicates that the original bundles of SWNTs disintegrate into individual tubes. The resulting *s*-SWNTs give black-colored solutions in chlorinated and aromatic hydrocarbons, and in CS_2. An initial reactivity study revealed that dichlorocarbene can be added to the walls of soluble SWNTs. Future investigations will show if the solution-phase wall chemistry of *s*-SWNTs will eventually rival that of the fullerenes. Further research in this area will certainly address the use of *s*-SWNTs as precursors for nanotube-based copolymers or as novel ligands in unusual transition metal complexes.

Another intriguing possible application is the use of covalently functionalized nanotube tips to probe biological systems on a nanometer scale. The ligand–receptor interaction of biotin–streptividin[23] was chosen to illustrate this approach. Nanotube tips covalently modified with biotin ligands were prepared by forming amide bonds between the carboxylic acid end groups and 5-(biotinamido)pentylamine. Subsequent force-displacement measurements carried out on mica surfaces containing immobilized streptividin showed well defined binding force quanta of about 200 pN per biotin–streptividin pair (Figure 13). No adhesion was regis-

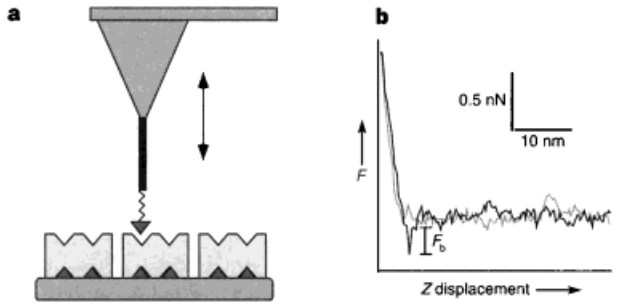


Figure 13. Ligand-modified nanotube tips as biological probes. a) Schematic diagram of a nanotube tip functionalized with a biotin ligand (black triangle) interacting with immobilized streptividin protein receptors (light-grey blocks); b) force–displacement curve recorded with a biotin-modified nanotube tip on the streptividin surface (F_b indicates the binding force) (reprinted with permission from *Nature*[21a]).

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tered in control experiments using unmodified carbon nanotube tips.

According to these results it appears quite possible to attach individual active ligands, proteins or other macromolecules to the ends of carbon nanotube tips and to create high-resolution maps of binding domains on proteins or membranes by using such functionalized nanotube probes. Another area where these nanotube tips may be successfully employed is the imaging of self-assembled polymeric and biological materials. Exciting future application could become reality if one could attach metal catalysts to the carbon nanotube end. Future research will show if such "magic wands" can be used to modify or create structures at the molecular scale. In any event an entire new branch of molecular technology will emerge from the chemistry and physics of carbon nanotubes.

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