Functional Covalent Chemistry of Carbon Nanotube Surfaces

By *Xiaohui Peng* and *Stanislaus S. Wong**

In this Progress Report, we update covalent chemical strategies commonly used for the focused functionalization of single-walled carbon nanotube (SWNT) surfaces. In recent years, SWNTs have been treated as legitimate nanoscale chemical reagents. Hence, herein we seek to understand, from a structural and mechanistic perspective, the breadth and types of controlled covalent reactions SWNTs can undergo in solution phase, not only at ends and defect sites but also along sidewalls. We explore advances in the formation of nanotube derivatives that essentially maintain and even enhance their performance metrics after precise chemical modification. We especially highlight molecular insights (and corresponding correlation with properties) into the binding of functional moieties onto carbon nanotube surfaces. Controllable chemical functionalization suggests that the unique optical, electronic, and mechanical properties of SWNTs can be much more readily tuned than ever before, with key implications for the generation of truly functional nanoscale working devices.

1. Introduction

The breadth and range of research into carbon nanotubes has expanded greatly over the past several years. Once considered a novelty, carbon nanotubes have become a key foundational material for the nanotechnology revolution for a number of reasons. From a purely structural perspective, a carbon nanotube is merely a rolled-up graphitic sheet, a one-dimensional manifestation of carbon elegantly packaged as a hollow, cylindrical motif. Yet, the deceptively simplistic act of rolling up that graphene sheet is associated with a number of possible and distinctive conformational permutations and that fact has a profound and complex effect on the physical properties of that tube.

For instance, the diameter and helicity of a defect-free single-walled carbon nanotube (SWNT) can be uniquely characterized by the roll-up vector, $\mathbf{c}_h = n\mathbf{a} + m\mathbf{b} = (n, m)$, connecting crystallographically equivalent sites on a two-dimensional (2D) graphene sheet, where **a** and **b** are the graphene lattice unit vectors and n and m are integers. Each pair of integers (n, m) defines a different way of rolling up the graphene sheet to form a carbon nanotube. Electronic band structure calculations predict that the (n, m) indices will determine whether a SWNT is a metal or a semiconductor.[1–5] To first order, (n, 0) or zigzag SWNTs will exhibit two distinct types of behavior. Nanotubes will be metallic when $n/3$ is an integer, but semiconducting when that ratio is nonintegral. Thus, as $\mathbf{c}_h$ rotates away from (n, 0), chiral (n, m) SWNTs are possible with similar electronic properties to zigzag tubes. When $(2n + m)/3$ is an integer, the tubes are metallic; otherwise, they are semiconducting. If $\mathbf{c}_h$ is rotated 30° relative to (n, 0), $m = n$. These (n, n) or armchair tubes are metallic. Zigzag and armchair tubes with wrapping angles of 0 or 30° are referred to as achiral tubes. SWNTs with intermediate wrapping angles are designated as chiral tubes. Both (n, 0) and (n, n) nanotubes have especially high symmetry and exhibit a mirror symmetry plane normal to the tubule axis.[6] In other words, their structure determines their electronic behavior.

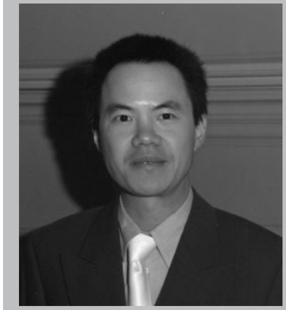
Due to these unique electronic properties, carbon nanotubes have been considered as attractive candidates for a number of diverse photochemical and electronic applications, ranging from molecular electronics, photovoltaic devices, to field effect transistors. In addition, nanotubes possess intrinsic advantages including high surface area, structural flexibility, and high mechanical strength; in fact, they might be stiffer and stronger than potentially any other known material with implications for the design of high-performance composite materials. It is not surprising therefore that nanotubes are thought to have a host of wide-ranging, potential applications including as catalyst supports in heterogeneous catalysis, field emitters, high-strength engineering fibers, sensors, actuators, tips for scanning probe microscopy, gas storage media, and as molecular wires for the next generation of electronics devices.[7–15] Nonetheless, there still is a huge contrast between the promising potential and tentative reality of using nanotubes in diverse, practical applications on a widespread scale.

---

[*] Prof. S. S. Wong, X. Peng
Department of Chemistry,
State University of New York at Stony Brook
Stony Brook, NY 11794-3400 (USA)
E-mail: sswong@notes.cc.sunysb.edu
Prof. S. S. Wong
Department of Materials and Chemical Sciences,
Brookhaven National Laboratory
Building 480, Upton, NY 11973 (USA)
E-mail: sswong@bnl.gov

DOI: 10.1002/adma.200801464

Xiaohui Peng is currently a doctoral student in Chemistry at the State University of New York at Stony Brook, under the supervision of Prof. Stanislaus S. Wong. She earned a B.Sc. in Chemistry from Nanjing University in 2006. Her research interests include devising new strategies for chemical functionalization of carbon nanotubes, probing the synthesis and characterization of carbon nanotube-based materials, as well as understanding the electronic and optical properties of these hybrid nanomaterials.



Stanislaus S. Wong is Associate Professor in Chemistry at the State University of New York at Stony Brook with a joint appointment at Brookhaven National Laboratory. He and his group have wide-ranging interests in nanoscience, including the rational chemical functionalization of carbon nanotubes, the synthesis and characterization of noncarbonaceous nanostructures (such as titanates, ferrites, fluorides, tungstates, and zirconates), the development of synchrotron-based techniques for nanoscale characterization, and the use of probe microscopy to initiate localized chemistry.

1.1. Challenges in Nanotube Processing

There are of course legitimate concerns associated with nanotube toxicity and biocompatibility, which still are being addressed. Nevertheless, the fact that nanotubes are being seriously considered as biosensors as well as drug delivery vehicles suggests that progress is being made in dealing with these problems. From a materials chemistry perspective, the key issues are batch-to-batch irreproducibility, poor processability, and lack of reliability of as-prepared carbon nanotube samples. These seem to be present no matter whether the nanotubes were generated by chemical vapor deposition, pulsed laser vaporization, or arc discharge processes. First, strong van der Waals interactions among pristine nanotubes can result in their bundling and aggregation, preventing their facile individualization. Second, nanotubes maintain notoriously poor solubility in aqueous media as well as in organic solvents. Third, as-prepared nanotubes tend to be contaminated with impurities such as metal catalyst particles, amorphous carbon, and other carbonaceous species. Fourth, there is an inherent variability and broadness in the length, diameter, and chirality distribution of these tubes. All of these factors are detrimental to the ultimate performance of carbon nanotubes. Of course, the ultimate goal would be to isolate a ‘‘bottle’’ of nanotubes consisting exclusively of a monodisperse population of tubes of one specific chirality and diameter. However, that vision is still as yet unattainable. A number of groups can generate samples that are ‘‘enriched’’ in either metallic or semiconducting tubes using diverse, but not necessarily standard, techniques based on chemical as well as physical separation protocols.

Hence, given these challenges with ‘‘pristine’’ tubes, use of chemistry is still one of the most effective means for manipulating and processing nanotubes, again with the goal of gaining reproducibility in handling these materials for eventual routine use and processing in device applications. At this stage, a number of key conclusions about nanotube reactivity are evident. First, nanotubes tend to be most reactive at their tips;[16] this enhanced chemical reactivity is a consequence of a greater propensity for defects such as pentagonal rings at nanotube ends. Another way of visualizing this issue is that the end caps of the carbon nanotubes resemble a hemispherical fullerene. Fullerene reactivity is primarily driven by the strain relief, which arises from pyramidalization at the carbon atom. Second, it turns out that in SWNT sidewalls, π-orbital misalignment between adjacent carbon atoms plays a larger influence in determining overall reactivity.[17,18] This misalignment, associated with bonds at an angle to the tube circumference (i.e., bonds that are neither parallel to nor perpendicular to the tube axis) is the origin of torsional stain in nanotubes, and the relief of this strain controls the extent to which addition reactions occur with nanotubes. Since π-orbital misalignment as well as pyramidalization scale inversely with tube diameter,[19] smaller diameter tubes are expected to be more reactive than larger diameter tubes.

The point is that nanotubes are susceptible to and can be reliably modified by chemical treatments. In one of the simplest examples, treatment of nanotubes in HNO_3 introduces oxygenated groups such as carboxylic acid groups onto the tips and defect sites of nanotube surfaces, cutting them into shorter ‘‘pipe’’ lengths and improving their solubility in organic solvents[20] and even in water,[21] thereby leading to a stable dispersion[21] of these materials. Additional analysis showed that acid treatment was selectively reactive toward smaller diameter tubes and could also improve overall purity by removing metal catalysts and amorphous carbon. Moreover, the conductivity of these particular tubes could potentially be enhanced[22,23] as it depends primarily upon the axial density of vacancy-carboxyl pairs. Furthermore, the higher resulting surface acidity of the functionalized nanotubes could also have an impact on their catalytic behavior.[24] Incidentally, treatment of nanotubes with ozone has been proposed as a means of their purification, controlled oxygenation, and rational sidewall functionalization.[25–30]

In the current Progress report, as in a prior Review,[31] we focus primarily on covalent methodologies for nanotube functionalization because of the intrinsic flexibility of introducing a variety of chemical moieties onto the ‘‘bare’’ surface of nanotubes with the explicit goal of tailoring physicochemical properties of nanotube surfaces. Moreover, covalent functionalization of carbon nanotubes can readily deal with fundamental issues of purification, solubilization, and processing, as we have previously discussed. We will separately discuss strategies primarily directed at the ends as well as at the sidewalls of these materials, as controllable spatially localized derivatization is essential for advances in functionalized material applications.

1.2. Theme of the Progress Report

The theme of this Progress Report is therefore to deduce how chemistry can be and has been used to nondestructively introduce practical functionality into nanotubes. The operative term is ''nondestructive,'' as it is well known that extensive formation of carbon-heteroatom bonds will alter a sp^2-hybridized configuration to that of a sp^3-hybridized structure, thereby resulting in disruption of the pseudo-one-dimensional lattice of carbon nanotubes with an accompanying loss of favorable optoelectronic properties. In this Progress Report, we therefore, explore advances in the formation of nanotube derivatives that essentially maintain and even enhance their performance metrics after chemical modification. For instance, chemical modification by $SOCl_2$ of an entangled network of purified SWNTs can improve conductivity by a factor of 5 at room temperature and increase toughness by an order of magnitude.[32] We especially highlight molecular insights (and corresponding correlation with properties) into the binding of functional moieties onto carbon nanotube surfaces. Because of the huge amount of work in this area, this Report will not necessarily be comprehensive but will at least be representative of overall progress in the field.

1.3. Tools of the Trade

A number of different analytical tools have been used to characterize the degree of functionalization of carbon nanotubes, including conventional microscopy techniques (such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM)), and optical protocols such as Raman spectroscopy and UV–visible–near IR spectroscopy. It has been reported though that AFM and STM data on the same system[33] will sometimes yield contradictory information about the extent of nanotube functionalization.

Regarding optical characterization, the electronic density of states of SWNTs possesses spike-like features known as van Hove singularities. Optically allowed transitions between these features can typically be observed in the UV–visible–near IR region.[34] For the specific case of commercial HiPco (high-pressure CO conversion) tubes, the primary features represent transitions between the first pair of singularities (M_{11}) in metallic tubes as well as between the first and second pairs (S_{11} and S_{22}) of singularities for semiconducting tubes. The point is that rigorous sidewall functionalization, for example, can disrupt the periodicity of the intrinsic conjugated sp^2-hybridized electronic structure of the SWNTs, and hence perturb these transitions.[35] Moreover, features in the far-IR have been ascribed to curvature-induced energy gaps in nonarmchair metallic nanotubes.[36]

Traditionally, Raman spectroscopy is one of the most powerful methods for probing the extent of covalent sidewall functionalization. Covalent binding of addends characteristically affects the intensity ratios of SWNT Raman bands. The most noticeable change is an increase in the intensity of the D band, which arises from the generation of sp^3 C atoms as defects in the sidewalls. The intensity ratio between the D band and the G band can therefore be taken as indicative of the extent of functionalization. However, it has been recently reported that in addition to the interpretative issue of an asymmetric Fano line shape of the G band peak, most metallic tubes also exhibit significant D-band intensities even within the same sample and that this complicating difference between metallic and semiconducting tubes arises from a double resonance process.[37] Aggregation effects have been purported to affect these Raman signals as well.[38]

The complementarity of other techniques cannot be overly emphasized. Luminescence spectroscopy and microscopy have become convenient techniques for probing the dispersion of functionalized nanotubes in polymeric nanocomposites where Raman data have been difficult to collect.[39] Sun and co-workers have found, for instance, that there are strong luminescence emissions associated with well-dispersed carbon nanotubes in most of these oligomeric functionalized samples, which they attribute to trapping of excitation energy by defect sites in the nanotube structure that become increasingly passivated upon functionalization.[40] Steady-state and time-resolved emission experiments have been used to determine how chemical functionalization and different degrees of oxidation affect the emission behavior of SWNT samples.[41] Moreover, elemental analysis techniques, such as X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy, are effective at determining the presence of metal particulates as well as yielding quantitative data about oxygen-to-carbon ratios and the presence of functional groups (such as carboxyl, carbonyl, aldehyde, and alcohol),[42] whereas thermogravimetric analysis (TGA) has been efficient at deducing the nature of amorphous carbon and other carbonaceous impurities. The reversibility of sidewall functionalization reactions (e.g., with diazonium) has been previously probed using conductance measurements.[43]

2. End and Defect Site Chemistry

2.1. Molecular Moieties

Amidation and esterification reactions have been some of the most common approaches used for linking molecular moieties onto oxygenated groups at the ends as well as the defect sites of oxidized carbon nanotubes. What has been interesting has been the range of chromophores, with intrinsically tunable optoelectronic properties, that have been covalently anchored onto SWNT surfaces for electronic and solar energy conversion applications, and the concomitant collection of rate constants and other data associated with fundamentally significant charge transfer processes. All of this work has implications for the rational design of light harvesting assemblies and optoelectronic devices, which will assist in moving forward toward the development of alternative energy sources and storage mechanisms.

In a classic example, pyrene has been ''tethered'' onto SWNTs via esterification of bound carboxylic acids on the nanotube surface to introduce a photoactive functionality. Indeed, the pyrene monomer excited state, initially long-lived as an unbound state, was found to be significantly quenched by two competing processes of ''intramolecular'' excimer formation and energy transfer to the SWNT, which were dependent on the tether length used[44] as well as on the density of pyrene units themselves.[45] That is, the spatial proximity of the SWNTs, acting as acceptors for an excited-state energy transfer from the tethered pyrenes,[46] results in an intramolecular quenching of the pyrenyl singlet excited state.[47] Interestingly, short, processed SWNTs, to which a pyrylium phtotsensitizer has been attached through an ethylthiopropylamide tether, show a so-called ''photoinduced solubility'' of an order of magnitude as compared with unfunctionalized SWNTs. Presumably, this observation can be attributed to debundling of tubes, arising from charge separation[48] produced by photoinduced electron transfer from the SWNTs to the pyrilium (Py) subunits and thereby resulting in a positive charging of the nanotube walls (Fig. 1).

The photo-optical behavior of additional molecular structures attached to SWNTs has also been probed. For instance, in an early experiment, simple esterification (with *n*-pentyl esters) of acid-purified SWNTs was reported to yield a sample that was not only soluble in organic solvents but also exhibited a high-quantum yield, short-lived (sub ns) photoluminescence.[49] Second, fluorescence from naphthalimide moieties covalently bound to SWNTs was found to be significantly quenched.[50] Third, asymmetrically substituted viologens have been covalently anchored to SWNTs through an ester linkage and studied by spectroscopy. The quenching constant of the SWNT emission by viologen was estimated to be about 2 orders of magnitude higher than the diffusion coefficient, suggesting quenching arising from the formation of a nonemissive viologen–SWNT complex.[51] With obvious energy storage implications, using methyl viologen radicals, a different group estimated that one could store as much as one electron per 100 carbon atoms of a SWNT.[52] Fourth, nanoconjugates containing tetrathiafulvalene (TTF) or π-extended TTF(exTTF) and SWNTs modified by HNO_3 and H_2SO_4/H_2O_2 have been formed using an esterification reaction. In this system (Fig. 2), by altering the relative electron donor–acceptor separation or by integrating different electron donors, control over the electron transfer in SWNTs was claimed.[53]

2.2. Bio-inspired Moieties

A number of key biological species, including antigen,[54] biotin,[55] and peptide nucleic acid,[56] have been attached either to the carboxylic end groups of SWNTs in the presence of carbodiimide agents such as EDC(1-ethyl-3-(3-dimethylamino propyl)carbodiimide) or DCC (dicyclohexylcarbo-diimide), or to acyl chloride termini localized at the ends of SWNTs. These reactions can proceed either with or without the aid of a linker molecule such as ethylenediamine.[57] For example, biotin derivatives containing terminal amino groups have been covalently attached to oxidized SWNTs via an amidation reaction. The resulting biotin-functionalized SWNTs, upon incubation with fluorescein-labeled streptavidin and both human promyelocytic leukemia (HL60) and human T (Jurkat) cells, were used to investigate the cellular uptake of SWNTs with protein via the endocytosis pathway.[55] Likewise, in order to covalently attach flavin mononucleotide (FMN) to the surface of SWNTs, a derivative, i.e., flavin pentyl H-phosphonate, was reacted with N-*t*-Boc protected aminohexylalcohol in the presence of EDC, followed by oxidation using I_2 to generate an N-*t*-Boc protected FMN. The attachment of FMN (Fig. 3) onto SWNTs was realized via the formation of amide bonds between the amino terminus of the FMN analog and free carboxylic groups on the surface of the SWNTs.[58] Photoluminescence and chemical redox behavior of FMN–SWNT conjugates both in the presence and absence of sodium dodecyl sulfate (SDS) surfactant suggested that SDS preserved FMN luminescence, presumably due to its blocking of unfavorable π–π interactions between the isoalloxazine ring of FMN and the nanotube sidewalls.

Other groups have either coated peptides[59] with selective affinity for SWNTs onto their surfaces, or bound proteins[60,61] such as either ferritin or BSA onto oxidized SWNTs via an amide linkage in aqueous solution. In these latter studies, the biological activities of the attached moieties were confirmed but the electrical activity of the functionalized nanotubes was not measured. Moreover, enzymes, such as horseradish peroxide, subtilisin Carlsberg, and chicken egg white lysozyme, have been covalently conjugated with SWNTs. Examination of the structure of these immobilized enzymes as well as related enzyme kinetics revealed that enzymes attached to SWNTs retained a high fraction of their native structure and activity.[62]

Recently, our group investigated the biocompatibility, specificity, and activity of a ligand–receptor–protein system (Fig. 4) covalently bound to oxidized SWNTs as a model proof-of-concept for employing such SWNTs as biosensors.[63] Specifically, SWNTs were functionalized under ambient conditions with either the Knob protein domain from adenovirus serotype 12 (Ad 12 Knob), or its human cellular receptor, the CAR protein, via diimide-activated amidation. The density of proteins on individual tubes was estimated to be up to 1 per 20 nm, as observed by AFM.

We confirmed the biological activity of Knob proteins immobilized on the nanotube surfaces using its labeled conjugate antibody. Moreover, the observed fluorescence upon attachment of fluorescently labeled Knob, which interacts specifically with

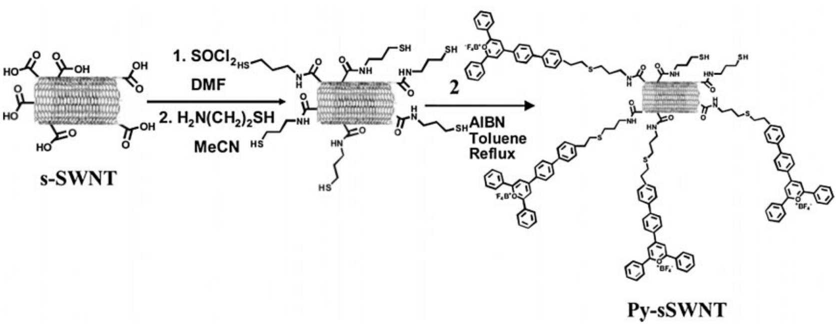


Figure 1. Synthetic routes for the preparation of Py–sSWNT. Reprinted with permission from [48]. Copyright 2007 American Chemical Society.

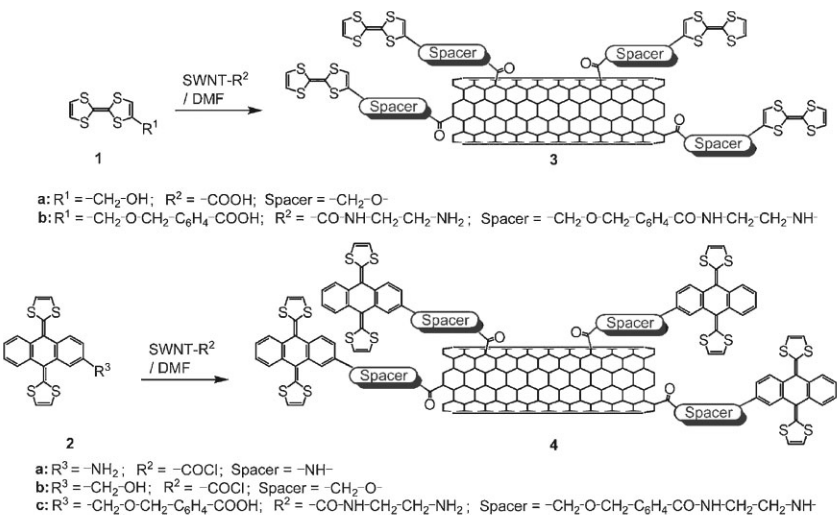


Figure 2. Synthesis of TTF- and exTTF-functionalized SWNTs. Reprinted with permission from [53].

CAR, as opposed to a negative control protein, YieF, which is not specifically recognized by biologically active CAR proteins, suggested the maintenance of the activity and specificity of bound CAR on the SWNT surface. In addition, current–gate voltage (*I*–*V*) measurements on a dozen nanotube devices explored the effect of protein binding on the intrinsic electronic properties of the SWNTs, and also demonstrated the devices' high sensitivity in detecting protein binding events due to a perceptible decrease in current upon protein attachment. By contrast, the recovery of electrical signals upon extended washing of noncovalently CAR-functionalized SWNTs suggested the importance and reliability of the covalent protein binding process.[63] Those interesting results provided evidence that covalent attachment of proteins onto SWNTs can afford a viable strategy toward developing specific quantitative biosensors.

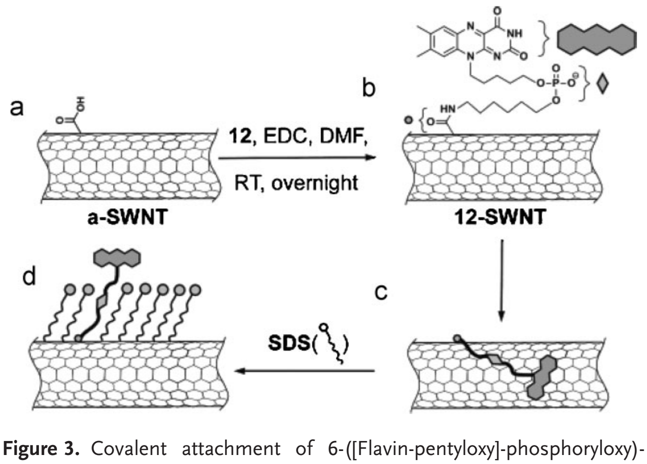


Figure 3. Covalent attachment of 6-([Flavin-pentyloxy]-phosphoryloxy)-hexyl-ammonium-trifluoro acetic acid salt (**12**) to acid-treated SWNTs a, b) and Flavin-tethered SWNTs and its conformation in the absence c) and presence d) of sodium dodecylsulfate (SDS). Reprinted with permission from [58]. Copyright 2008 American Chemical Society.

Electrochemical immunosensors (Fig. 5) using SWNT forest platforms with multi-label secondary antibody-nanotube bioconjugates have also been reported[64] for highly sensitive detection of a cancer biomarker in serum and tissue lysates with a lower limit of 4 pg mL^{-1} noted for prostate specific antigen in 10 μL of undiluted calf serum that surpassed the performance of conventional immunoassay methods. In addition, optical sensing,[65] namely through measuring the sensitivity and extent of a fluorescence recovery process, has been employed as a mechanism of operation for SWNT biosensors based on a redox–active dye–ligand conjugate; the methodology has been able to attain nanomolar sensitivity with high specificity for the target ligand.

2.3. Inorganic Interfaces to SWNTs

The reactivity of SWNTs toward metal complexes is substantially different from that of fullerenes, even though both possess a nonplanar sp^2 configuration. Curvature effects and different degrees of local strain between the two structures likely account for the observed differences in behavior. Specifically, the presence of five-membered cyclopentadienyl-like rings in C_{60} substantially enhances the affinity of (6,6) bonds in coordinating metal complexes and allows for strong back donation in the resulting adducts, thereby promoting their stability. However, theoretical calculations on molecular fragments replicating SWNT surface curvature indicate that, unlike in the case of fullerenes, five membered rings are not present to stabilize π^* ligand orbitals and hence, backbonding interactions are much weaker in these systems.[66] In fact, the elimination of pyramidalization of carbon atoms in fullerenes as well as the relief of local and global strain on η^2 coordination have been the driving forces for metal-complexation reactions of fullerenes.[67] The reactivity of SWNTs with respect to metal coordination compounds has not been as straightforward as well, though we have found that coordination at oxygenated sites appears to be a favorable mode of bonding.

Functionalization of oxidized nanotubes with Vaska's complex[68] at their ends and defect sites renders nanotubes soluble and stable in organic solution, originating from exfoliation of large crystalline ropes to smaller bundles and individual tubes, and thereby enabling further exploitation of their wet chemistry. Theory has confirmed that the transition metal center coordinates to carbon atoms belonging to pentagonal rings, as in topological defects or end caps.[69] Moreover, as the functionalized tubes are easily recoverable from solution, this finding has had significant scientific and economic implications for nanotubes as reusable catalyst supports, particularly for expensive catalyst materials. Similar behavior has also been demonstrated for Wilkinson's compound,[70] which is a Rh-based system, useful in the recyclable catalytic hydrogenation of alkenes such as cyclohexene to cyclohexane. Vanadyl salen complexes covalently anchored to SWNTs have additionally been used as heterogeneous catalysts for the cyanosilylation of aldehydes with trimethylsilylcyanide.[71]

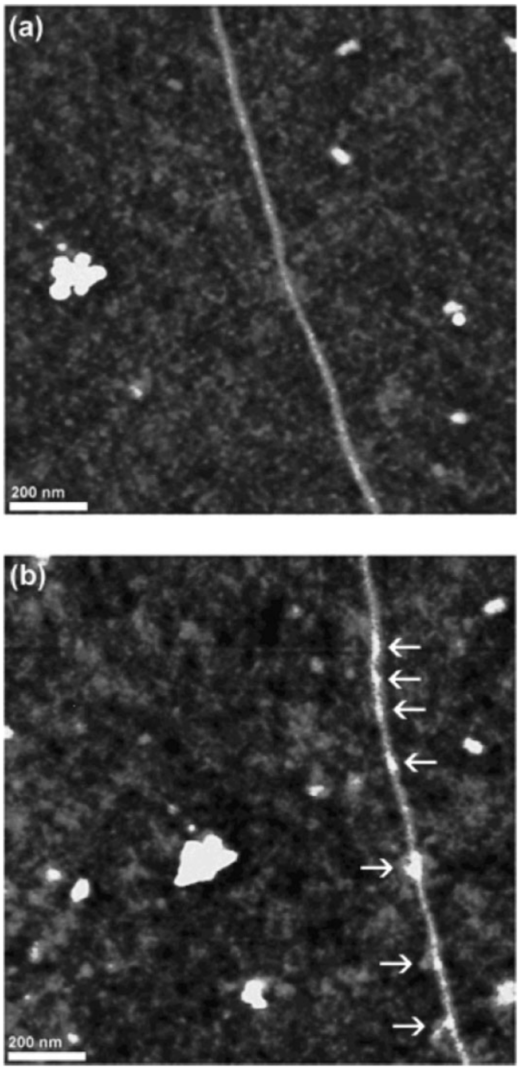


Figure 4. a) AFM height image of single-walled carbon nanotubes on a Si/SiO_2 substrate after oxidation. The *z*-axis color scale is 10 nm. b) AFM height image of the same nanotube after the attachment of the CAR protein and subsequent exposure to Knob protein. Arrows indicate seven main sites along the nanotube's length where the CAR + Knob complex is bound to the nanotube's surface. The vertical *z*-axis color scale is 10 nm. The images were low-pass filtered for clarity. Reprinted with permission from [63]. Copyright 2007 American Chemical Society.

Ruthenium-based compounds[72] as well as rigid dendritic ruthenium complexes[73] have been utilized to generate interconnects and assemblies of nanotubes. In the latter case, nanotube ends were strongly and specifically functionalized with optically active, rigid supramolecular complexes of enantiometrically pure ruthenium metallodendrimers, measuring 5.8 nm in dimension.[73] Moreover, covalent attachment[74] of ruthenium(II)-tris(2,2′-bipyridine) to SWNTs rendered them sensitive to light that had been absorbed by the ruthenium complex and made the nanotubes persistently photoconductive with a quantum yield of 0.55, with potential applications in optical switches, photodetectors, electrooptical information storage devices, and chemical sensors.

Furthermore, in an initial study in our laboratory, oxidized, cut SWNTs were reacted with lanthanide salts containing Eu, La, and Tb. These studies found that the lanthanide ions[75] likely coordinate to SWNTs through a disruption of hydrogen bonding in bundles of oxidized SWNTs. Adducts were analyzed using FT-IR, Raman, and photoluminescence spectroscopy and were structurally characterized using AFM and TEM, along with energy-dispersive X-ray spectroscopy (EDS). In these systems, SWNTs can serve as electron acceptors,[76–78] and hence, can act as an energy sink in an excited-state energy transfer mechanism. Indeed, upon coordination of these lanthanide ions to oxidized SWNTs and subsequently, upon relaxation after excitation, some degree of energy transfer is expected from the metal to the low-lying excited states in the visible and near-IR regions of the SWNTs, which thereby resulted in a decreased intensity in the intrinsic emission of the lanthanide ions as a function of increased reaction time and concentration. All of these results have implications for potential sensor and imaging applications.

With respect to Si-containing complexes, organosilanes have been previously used as coupling agents on hydroxylated surfaces for generating organic coatings,[79] with the idea that the electrical properties of carbon nanotubes can be appropriately adjusted through rational chemical functionalization. For instance, the application of a dc electric field can enhance the assembly of silane-modified SWNTs into ordered films with rectifying diode behavior.[80] In addition, pristine SWNTs initially modified with carboxylic groups and subsequently functionalized with (3-glycidoxypropyl)trimethoxysilane in a sol–gel process have been found to have improved dispersability in a silica matrix, as well as better mechanical properties (e.g., 33% increase in stress and 53% increase in toughness) and enhanced electron-transfer kinetics.[81] Recently, our lab has reported[82] on the effective silylation of raw, pristine SWNTs, a work inspired by theoretical studies[83,84] claiming that the $(2+1)$ cycloaddition of silylene on nanotube sidewalls is site-selective and diameter-specific, in addition to favoring opened structures.[85,86]

The silylation protocol (Fig. 6) developed in our laboratory did not require harsh oxidative methods. Specifically, SWNTs were functionalized at their ends and sidewalls (i) with trimethoxysilane and in a separate experiment, (ii) with hexaphenyldisilane under Schlenk line conditions in the presence of UV irradiation. Whereas microscopy results clearly showed that the functionalization reaction was structurally nondestructive to the tube integrity, spectroscopy data provided evidence for chemical attachment of organosilanes onto the carbon nanotube surface. Moreover, Raman analyses demonstrated selective reactivity of predominantly smaller-diameter semiconducting nanotubes. For example, semiconducting (7, 5) and (9, 2) tubes with a diameter of 0.84 and 0.79 nm, respectively, were shown to exhibit a dramatic decrease in intensity of the radical breathing mode (RBM) upon silylation. UV–Visible data also yielded evidence for selectivity and functionalization.

Finally, SWNTs have also been used as substrates for the deposition of metals by electron-beam evaporation, resulting, for the cases of Au, Al, Pb, and Fe, in the formation of discrete particles on nanotubes due to a weak interaction between metals

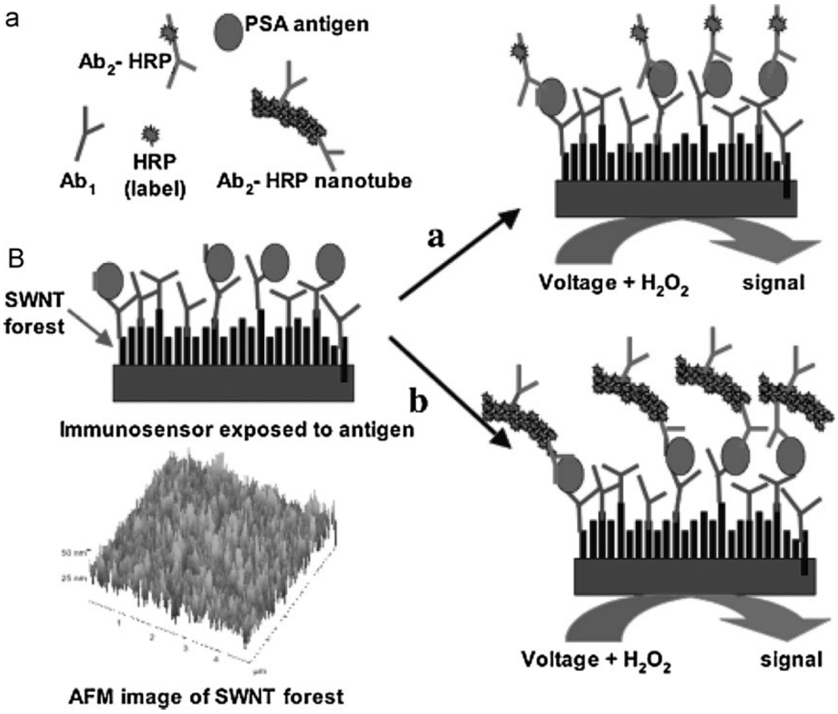


Figure 5. Illustration of detection principles of SWNT immunosensors. Reprinted with permission from [64]. Copyright 2006 American Chemical Society.

and nanotubes.[87] Acid groups on treated SWNTs can act as nucleation sites for a well-dispersed deposition of Pt clusters.[88] With Ti, Ni, and Pd, quasi-continuous coatings are possible, resulting in the formation of nanotube-supported metal nanowire structures.[89] There is a rich body of the literature on the synthesis of and applications associated with nanotube-quantum dot/metal nanoparticle heterostructures; this work will be covered in a separate future article by our group.

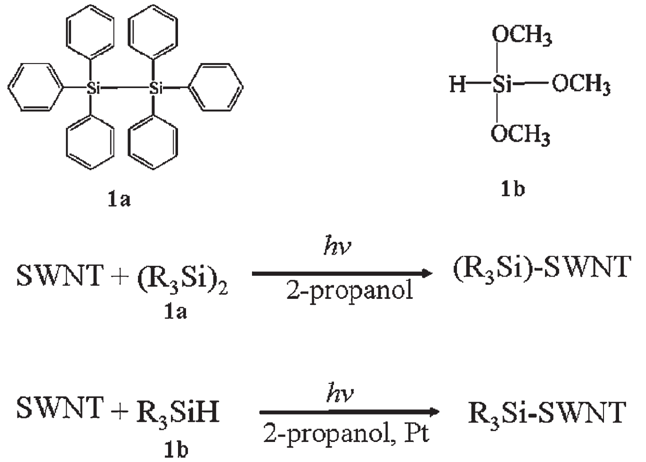
3. Covalent Sidewall Functionalization

The reactivity of SWNTs toward sidewall addition depends on the diameter of the tubes as well as on the pyramidalization angle of the tube's carbon atom where the cycloaddition reaction takes place. Indeed, the convex surface[90] is more reactive than the concave one and the difference in reactivity increases with an increase in pyramidalization angle and a decrease in the tube diameter. Moreover, the reactivity of the convex surface is enhanced by the pronounced exposure of the hybrid π orbitals from the exterior surface which favors orbital overlap with incoming addends.[19]

Current synthetic efforts associated with sidewall functionalization have focused on utilizing polar, pericyclic, as well as radical reactions to construct carbon-carbon and carbon-heteroatom bonds on the surfaces of carbon nanotubes.[91] A typical reaction involves a cycloaddition, which is a pericyclic chemical reaction in which two π bonds are lost and two σ bonds are correspondingly formed. By analogy to fullerenes, the nature of the unsaturated π-electron system of carbon nanotubes allows for sidewall functionalization through diverse reactions including 1,3-dipolar and Diels–Alder cycloadditions.

3.1. Organic Functionalization Strategies

Direct addition to the unsaturated π-electron systems of SWNTs can also occur through a number of different reactions,[31,92–94] including (i) a (2 + 1) cycloaddition of nitrenes, where, in the presence of alkyl azidoformates, alkoxycarbonylaziridino-SWNTs can be formed as deduced by XRD, XPS, and Raman spectroscopy,[95,96] (ii) a (4 + 2) Diels–Alder cycloaddition of *o*-quinodimethane theoretically predicted[97] to be viable due to aromaticity stabilization at the corresponding transition states and products, and experimentally performed under microwave irradiation,[98] (iii) the addition of nucleophilic carbenes,[99] which have been theoretically probed using a two-layered ONIOM approach,[100,101] and (iv) a cyclopropanation process accomplished under Bingel reaction conditions, which can be visualized using AFM.[102] Many of these reactions can introduce functional groups such as alkyl chains, aromatic groups, dendrimers, crown ethers, and oligoethylene glycol units onto nanotube surfaces.[103] Moreover, all of these approaches have been assessed theoretically as means of purifying, opening sidewalls, and separating SWNTs diameter-specifically.[104,105] In addition, theoretical calculations[106] predict that nitrene and carbene (2 + 1) cycloaddition reactions on narrow-diameter tubes can recover, as a consequence of bond cleaving, the "ideal" conductance of original pristine tubes. Metallic tubes subjected to covalent sidewall functionalization of CCl$_2$ experience a band



$$\mathrm{SWNT} + (\mathrm{R_3Si})_2 \xrightarrow[\text{2-propanol}]{h\nu} (\mathrm{R_3Si})\text{-}\mathrm{SWNT}$$

$$\mathrm{SWNT} + \mathrm{R_3SiH} \xrightarrow[\text{2-propanol, Pt}]{h\nu} \mathrm{R_3Si}\text{-}\mathrm{SWNT}$$

Figure 6. Representation of typical reactions between SWNTs and appropriate silane precursors. Reprinted with permission from [82]. Copyright 2006 American Chemical Society.

gap opening as the functionalization concentration increases to 11% followed by a continuation of the bandgap trend with rising functionalization levels up to 33.3%.[107]

Functionalization of individual ultrashort (20–80 nm) SWNTs with malonic acid bis-(3-*tert*-butoxycarbonylaminopropyl)ester has been noted using Bingel chemistry (CBr_4/1,8-diazabicyclo[5.4.0]undec-7-ene).[108] Moreover, a recent report revealed that microwave-assisted modification of SWNTs by the Bingel reaction could not only improve their solubility but also preserve the intrinsic electronic properties of SWNTs, even at a moderate level of modification, estimated at one functional group per 75 carbon atoms along the sidewalls.[109] This result was in direct contrast with data expected from conventional sidewall functionalization (1 functional group per 10–100 carbon atoms) of SWNTs such as 1,3-dipolar cycloaddition involving azomethine ylide.[109] It was reasoned that the highly strained three-membered ring structure on the sidewalls, emanating from the Bingel reaction, yielded products with opened sidewalls in a type-II geometry, meaning that the plane of the three-membered ring was perpendicular to the long axis of the SWNT, thereby leading to the preservation of the sp^2 hybridized network of carbons along the nanotube sidewall. Conversely, when the plane of the three-membered ring structure was parallel to the long axis of the SWNT (type-I geometry), the electronic structure of the functionalized SWNTs was not as readily maintained.

A recent review article[110] has suggested that fluorinated nanotubes possess altered conductive and optical properties and that they are also useful precursors for various subsequent reactions. As such, fluorinated SWNTs can undergo Diels–Alder addition reactions with a wide range of dienes, resulting in a C: substituent ratio between 20:1 and 32:1, as proven by consistent IR, Raman, AFM, and ^{13}C NMR measurements.[111]

Recently, a novel, convenient cycloaddition approach,[91] using zwitterions, a class of dipolar species resulting from the addition of nucleophiles to activated electrophiles, has been reported as a means of functionalizing not only fullerenes but also carbon nanotube sidewalls. Essentially, this is a modular reaction involving an initial formation of a positively charged 5-member ring intermediate resulting from attack of a highly nucleophilic species, 4-dimethylaminopyridine (DMAP), in the presence of an electrophile, dimethyl acetylenedicarboxylate (DMAD). In the final step, the DMAP moiety is replaced with other nucleophiles, such as methanol and 1-dodecanol, to yield the desired functional group (such as alkyl groups), as shown in Figure 7. A high level of functionalization of up to one functional group per nine carbon atoms was deduced based on XPS and TGA data. In the case of 1-dodecanol utilized as the second nucleophile,[91] the resulting functionalized SWNTs showed significantly improved solubility in a variety of solvents including $CHCl_3$, CH_2Cl_2, THF, and DMF.

3.2. Azomethine Ylides

Derivatization based on 1,3-dipolar cycloaddition of azomethine ylides, generated by the condensation of an α-amino acid and an aldehyde, has been utilized to solubilize tubes in most organic solvents.[112] This functionalization technique; in particular, has also been employed for the purification of commercial HiPco SWNTs.[113] Nonetheless, one disadvantage of this initially versatile protocol is that it can be time-consuming and tedious. Recently, nanotubes were rapidly functionalized by using 1,3-dipolar cycloaddition of aziridines under solvent-free microwave-assisted conditions[114] that could reduce the reaction period to a few hours from several days. Indeed, microwave chemistry is often more efficient and involves less severe reaction conditions[109,114–116] as compared with conventional techniques.

Using azomethine chemistry, N-terminal protected amino acid[117,118] as well as a series of bioactive peptides[119,120] have been attached successfully onto ammonium-terminated triethylene glycol-modified CNTs through the formation of a covalent bond (Fig. 8). Moreover, it has been demonstrated that these peptide–SWNT conjugates are able to bioaccumulate in mammalian cells at levels of up to 10 μM,[121] without any noticeable signs of toxicity, suggesting that these functionalized carbon nanotubes have potential as drug delivery vehicles of biologically active molecules.

In addition to biological functionalization of nanotubes, derivatization through 1,3-dipolar cycloaddition of azomethine ylides has been shown to be a powerful methodology for chemically modifying SWNTs as well. For instance, using azomethine ylide groups with anchoring phenol structures has yielded functionalized nanotubes that, when dispersed in an epoxy/Novolac composite, can affect curing kinetics.[122]

A particularly intriguing set of experiments has recently been performed by the Prato group involving functionalization of photoactive chromophores which have yielded interesting photophysics with implications for the development of light harvesting architectures.[123] The idea has been to generate photocurrent generating devices based on nanotube templates. One theme has been to covalently couple electron-accepting SWNTs with electron–donating groups (such as ferrocene).[124] For instance, 1,3-dipolar cycloaddition of nitrile imines to the sidewalls of SWNTs has been used to synthesize two soluble, photoactive SWNTs containing *n*-pentyl esters at the tips and 2,5-diarylpyrazoline units at the walls of the tubes.[125] Photochemistry data were compatible with the occurrence of an electron transfer from electron rich substituents of the pyrazoline unit to electron acceptor termini including electron poor aryl rings and nanotube walls. In another case,[126] SWNTs sidewall functionalized via a Heck cross-coupling reaction of *p*-iodophenyl SWNTs with alkyl chains, dialkylamino, or anthracenyl moieties revealed the presence of photoinduced electron transfer to the SWNTs but the charge separated state was short-lived, decaying in less than 10 μs.

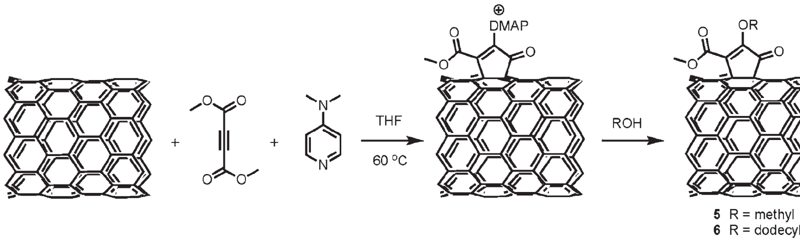


Figure 7. Modular approach toward SWNT functionalization. Reprinted with permission from [91].Copyright 2007 American Chemical Society.

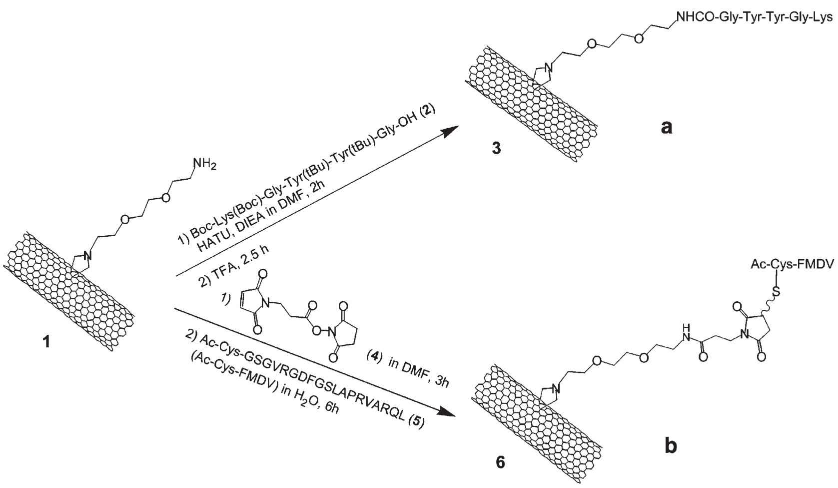


Figure 8. Synthesis of the peptide–carbon nanotubes via a) peptide fragment condensation and b) chemoselective ligation. Reprinted with permission from [119]. Copyright 2003 American Chemical Society.

With azomethine ylide chemistry, polyamidoamine dendrimers have been directly synthesized onto the surfaces of SWNTs by initially forming a pyrrolidine ring functionalized with a *n-tert*-butoxycarbonyl protected amine group through an azomethine ylide reaction followed by dendrimer construction, starting from ethylenediamine and methyl acrylate.[127] A photophysical study of the nanoconjugate between tetraphenylporphyrin moieties linked to the peripheries of these dendrimers and the dendrimer-functionalized SWNTs themselves suggested that the anticipated charge separation evolved from the excited porphyrin to the SWNTs, accompanied by a fast decay of the photoexcited porphyrin.[127]

In a separate experiment, phthalocyanines (Pcs), chromophores with intense red/near-IR absorption, have also been linked to Boc-protected SWNTs [128] in the presence of EDC, through the reaction of the terminal carboxylic acid groups of SWNTs with amino-functionalized Pcs. A significant quenching of the fluorescence of Pcs was observed due to electronic interaction between the photoexcited chromophore and SWNTs. In a further study, two additional strategies by means of cycloaddition and esterification were developed to functionalize SWNTs with Pcs addends (ZnPc).[129] Raman, IR, and TGA data supported the covalent modification of SWNTs. The occurrence of electron transfer from ZnPc to SWNTs was observed in transient absorption experiments, which confirmed the absorption of the one-electron oxidized ZnPc cation and the concomitant bleaching of the van Hove singularities typical of SWNTs; specifically, charge-separation and charge-recombination dynamics revealed a notable stabilization of the radical ion pair product presumably due to charge injection into the conduction band of the tubes.[130]

3.3. Diazonium Reaction

SWNTs have been chemically functionalized in situ by a thermally induced reaction with diazonium compounds, generated by the action of isoamyl nitrite on aniline derivatives.[131] Essentially, this reaction is thought to occur by injection of an electron from SWNTs into an aryl diazonium salt that then induces the formation of a reactive aryl radical, thereby releasing N_2 and resulting in the formation of a new SWNT-arene bond.[132] While the reaction was first done electrochemically, it was later shown that the diazotisation functionalization could also be achieved at high temperatures by refluxing the reaction mixture.[133,134] This procedure allows for a very high degree of functionalization (estimated to be 8–12% from TGA experiments) to be achieved. In addition to –F, –Cl, $-CO_2H$, $-NO_2$, and *t*-butyl functional groups, SWNTs have also been functionalized with reactive amine moieties using this generalized protocol.[135] In these reactions, comparison between Raman and optical absorption results reveals a dependence of the diazonium functionalization (up to 4.1%) on the nanotube diameter as well as charge transfer between the nanotube and the functional group.[136]

A solvent-free analog (Fig. 9) of this system has been reported, wherein this potentially large-scale reaction proceeds by either mechanical stirring or ball milling to yield highly functionalized nanotubes with high solubility (e.g., 0.03 mg mL^{-1} in THF).[137,138] The derivatization with arenediazonium has been studied mechanistically using GC-MS and XPS.[132] In particular, the reaction with 4-chlorobenzenediazonium has been proposed as a model electron-transfer reaction that is selective for metallic versus semiconducting tubes via a charge-transfer stabilization of complexes at the surfaces of the former.[139]

The Tour group later developed a means of functionalizing SWNTs in fuming sulfuric acid (oleum) to afford unbundled individual SWNT-arylsulfonic acids that did not require either surfactant or polymer-based prewrapping, centrifugation, or sonication.[140] A method was subsequently developed to create bulk quantities of oleum-treated water-soluble SWNTs containing multifunctional addends,

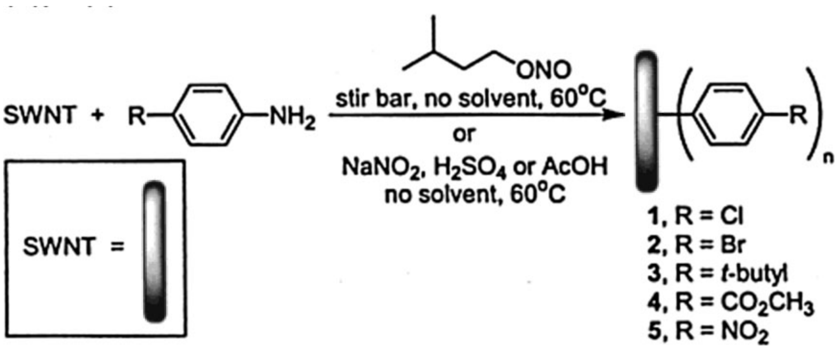
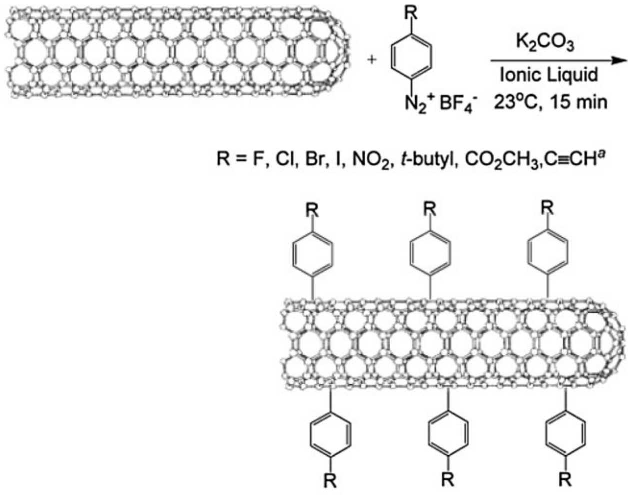


Figure 9. Solvent-free functionalizations performed with various 4-substituted anilines and isoamyl nitrite or sodium nitrite/acid. Reprinted with permission from [137]. Copyright 2003 American Chemical Society.

that avoided the further use of either high-powered sonication, centrifugation, or even oleum as the solvent. Using individualized SWNTs (initially generated from the oleum procedure though) followed by repetitive aqueous aryl diazonium reactions, multifunctional addends were introduced onto the SWNT surface, including biologically significant molecules or other structurally sensitive moieties that would not otherwise have been able to survive the intrinsically harsh strongly acidic conditions characteristic of oleum.[141] Moreover, SWNTs have also been functionalized in a mixture of 96% sulfuric acid and ammonium persulfate using sodium nitrite to produce intermediate diazonium salts from substituted anilines to yield unbundled functionalized SWNTs from bulk bundled SWNTs without using oleum.[142]

It was already known that aryldiazonium salts can react efficiently with individual, highly dispersed SDS-coated SWNTs in water to form aryl functionalized SWNTs.[134] A variation of this process was carried out using nonsurfactant-wrapped SWNTs ''on water'' in the presence of a substituted aniline and an oxidizing agent (such as sodium nitrite) under aqueous neutral or acidic pH conditions.[143] Recently, through the mediation of triazene, additional molecules of interest, including biotin, could be directly attached to the SWNT surface in a pH range of 2–10.[144] The use of either triazene (converted into diazonium in situ in the presence of HF)[145] or oligo(phenylene ethynylene) aryldiazonium salts[146] has also facilitated the covalent anchoring of functionalized SWNTs onto silicon surfaces, producing durable Si-SWNT nonmetallic molecular junctions useful for developing molecular electronic devices that do not possess metal electrodes in direct contact with molecular species and which may therefore obviate the need for metallic filaments.[147]

Moreover, the Tour group also devised an environmentally friendly methodology[148] for exfoliating and uniformly functionalizing SWNTs as individual tubes by grinding them for minutes at room temperature with aryldiazonium salts in the presence of ionic liquids and K_2CO_3 (Fig. 10). An ionic liquid consisting of p-butylbenzenediazonium ions and bis(trifluoromethanesulfonyl)amides was recently synthesized as a ''green'', low temperature medium for the solvent-free modification of carbon[149] and should be useful for future electrochemical applications[150] involving SWNTs. A room-temperature ionic liquid was used as a dispersal medium in which to homogeneously electrograft *n*-succinimidyl acrylate onto SWNT surfaces for the purposes of sensing and catalysis applications.[151] Interestingly, it turned out that when a buckypaper of SWNTs was wetted by an ionic liquid, its mechanical properties were affected so functionalization was likely coupled with a favorable improvement in performance.[152]



[a] The alkyne moiety was *meta*-substituted relative to the diazonium functionality.

Figure 10. Functionalization of SWNTs in ionic liquid using a mortar and pestle. Reprinted with permission from [148]. Copyright 2005 American Chemical Society.

3.4. Alkylation

Reductive alkylation of SWNTs yields sidewall functionalized tubes, such as dodecylated SWNTs, in which alkyl radicals are involved as intermediates.[153] In these reactions (Fig. 11), nanotubes are typically treated with lithium metal in liquid ammonia followed by the addition of either alkyl iodides[153], aryl iodides,[154] or aryl/alkyl sulfides.[155] The same group[156] has also broadened this reaction to the use of either lithium, sodium, or potassium in liquid ammonia to yield dodecylated tubes that are soluble in organic solvents. The fast electron transfer process from lithium to the nanotubes was associated with SWNT debundling, as observed by TEM and AFM.[153] Hence, beyond its obvious capability of introducing a number of functionalities, overall, this is an important protocol because it readily allows for chemistry to be performed at the single tube level. Specifically, upon addition of either the alkyl or aryl halide, radical anions were formed and subsequently dissociated to yield halide and an alkyl/aryl radical, which could then react with the SWNT sidewalls. In so doing, reduced tubes acquired a more pronounced nucleophilic character, thereby allowing for additional chemistry to be performed on their surfaces under less stringent reaction conditions. For example, these reduced SWNTs were noticeably reactive toward peroxides, even at room temperature.[157]

The ''radical'' approach is actually quite robust. For instance, alkylation of SWNTs often involves the use of free radicals, generated for instance by the decomposition of benzoyl peroxide in the presence of alkyl iodides, yielding phenyl radicals.[158] Chemisorption of phenyl rings through covalent bonding has been predicted to reduce thermal conductivity by over a factor of 3, due presumably to a reduction in phonon scattering length.[159] Many of these sidewall reactions have been characterized using Raman, FT-IR, and UV–visible–near IR spectroscopy as well as TGA/MS, TGA/FT-IR, and TEM data in addition to solid state ^{13}C NMR spectroscopy.[160,161] Free radicals (e.g., 4-methoxyohenyl-free radicals) have also been generated either by air oxidation of 4-methoxyphenylhydrazine hydrochloride[162] or by using a microwave-assisted approach with an optimal reaction time of 5 min.[163] SWNTs have been functionalized via one-electron reduction of benzophenone by potassium.[164] In another related study, irradiation of benzophenone (e.g., an aromatic ketone), benzhydrol, and SWNTs in benzene resulted in covalent attachment of benzhydrol to the sidewalls of SWNTs at a density of 1 molecule per 52 sidewall carbons.[165]

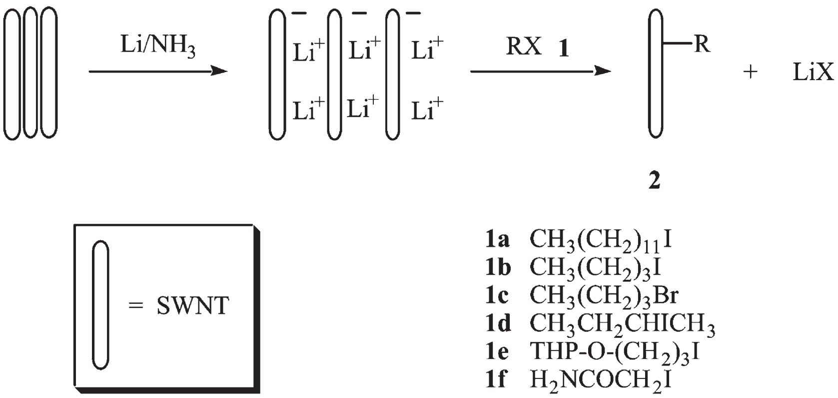


Figure 11. Functionalization of carbon nanotubes via reductive alkylation using lithium and alkyl halides in liquid ammonia. Reprinted with permission from [153]. Copyright 2004 American Chemical Society.

Alkyl groups can also be introduced through the (i) nucleophilic addition of *t*-BuLi to the sidewalls of the tubes, (ii) formation of negatively charged intermediates leading to debundling, and (iii) subsequent reoxidation of these intermediates to form neutral alkylated products (Fig. 12).[166] In the latter case, degrees of functionalization expressed as the carbon-to-addend ratio of up to 31 were attained, comparable to data from the Billups alkylation/arylation reaction.[134,153] Moreover, STM confirmed the presence of covalently bound *t*-butyl groups to the sidewalls, while Raman spectroscopy suggested a preferential reactivity of metallic tubes, due to the presence of electronic states close to the Fermi level, in this charge transfer reaction.[166] The reactivity for both metallic and semiconducting SWNTs toward the addition of organolithium and organomagnesium compounds was also found to be inversely proportional to the diameter of the tubes and was clearly dependent upon the steric demands of the addend.[167] Similar arguments have been made for both diazonium and osmylation reactions as potentially useful mechanisms for the separation of metallic versus semiconducting nanotubes.[168,169] In particular, with these classes of reactions, metallic SWNTs, due to their finite and readily available electron density at the Fermi level as compared with semiconducting tubes, are better able to stabilize the transition state involved, will consequently accelerate the forward rate of reaction, and hence will preferentially react, as compared with semiconducting tubes.

Sidewall-fluorinated nanotubes can also be alkylated by either reacting them with alkyl magnesium bromides in a Grignard synthesis or by reaction with alkyllithium precursors to yield sidewall-alkylated nanotubes, via a concerted, allylic displacement mechanism.[170] Covalent attachment to the sidewalls was confirmed by UV–Visible–near-IR spectroscopy,[171] wherein optical features originating from transitions between the van Hove singularities in the 1-D electron density of states of the tube disappear as the electronic structure becomes perturbed. Moreover, upon reaction with organic peroxides including benzoyl and lauroyl peroxide, phenyl and undecyl sidewall functionalized tubes can be produced, though the reactions occur faster with C$_{60}$.[172]

Polyacylation under Friedel–Crafts conditions is an excellent way of purifying and decorating nanotubes with a variety of alkyl, aryl, and fluoryl groups.[173] Though SWNTs can be functionalized under mild conditions by ball milling at room temperature in the presence of vapors of alkyl halides,[174] free alkyl radicals generated by decomposition of benzoyl peroxide in the presence of alkyl iodides have been more effective at derivatizing the sidewalls of small-diameter SWNTs with an efficiency as high as 20% as estimated by TGA.[158]

4. Impacts

It is clear that covalent chemistry can be used to manipulate SWNTs. Nonetheless, key challenges remain with generating defect-free functionalized nanotubes in large quantities, at low cost, and under reasonably mild reaction conditions (e.g., in terms of temperature, reaction time, reduction in reagent use, and formation of nontoxic byproducts). It should also be explicitly mentioned that while a definitive resolution of the issue of biological toxicity (especially long-term) of functionalized SWNTs has not as yet been achieved, preliminary data suggest that PEG-derivatized SWNTs are not harmful to mice[175] and that immune cell viability[176] is preserved even in spite of the presence of tubes functionalized by a 1,3-dipolar cycloaddition reaction. Furthermore, stable aqueous solutions of functionalized SWNTs were not obviously toxic to either murine fibroblasts[121] or to human promyelocytic leukemia cells.[177] Interestingly enough, for human dermal fibroblasts, the level of cytotoxicity actually decreased with increasing covalent sidewall functionalization.[178]

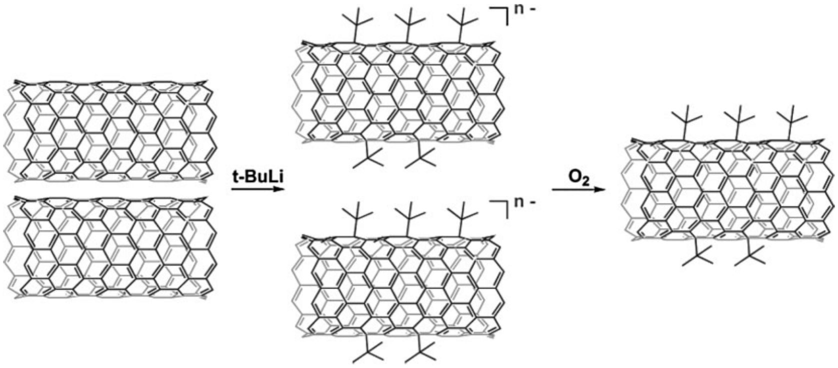


Figure 12. The nucleophilic–alkylation–reoxidation-functionalization of SWNT. Reprinted with permission from [166]. Copyright 2006 American Chemical Society.

From the perspective of sample quality control, perennial concerns such as resulting purity, degree/density of modification, and solubilization will always be intertwined with mastering the rational chemical functionalization of SWNTs. After all, covalent chemistry can alter the wetting behavior, the free energy, and hydrophobicity (Fig. 13) of a nanotube surface[179] with ramifications for its manipulation and additional processing. However, the ability to chemically design defectless-functionalized nanotubes from scratch and to predict their specific mechanical, transport, photoconductive, thermoelectric, electronic, optical, and catalytic behavior based on their modified structure remains elusive.

Nonetheless, nanotube chemistry, using a combination of chemical strategies we have discussed in this Progress Report, already plays a significant role in defining a practical range of potential applications, which we describe below. In one of the simplest cases, intermolecular carbon nanotube junctions can be formed by reacting chloride terminated nanotubes with aliphatic diamines.[180] In addition, thiolation of SWNTs offers a reliable and simple way for preparing functionalized tubes for nanoelectronic circuits.[181] Density functional theory studies have shown that crosslinking thiolated SWNTs with thiocarboxylic and dithiocarboxylic esters result in structures where the strength and stability of intertube bonds actually increases in the vicinity of defect sites.[182] There are additional case studies of situations, where chemistry has yielded substantive improvements in performance. Specifically, many of these approaches take advantage of the use of carboxylic acid residues immobilized onto SWNTs; in this regard, a recent paper proposed either a direct coupling of ethylenediamine with carboxylic acid groups or reduction of carboxyl groups to hydroxymethyl moieties followed by a subsequent transformation into aminomethyl groups as a means of creating amino-functionalized nanotubes for binding to (i) polymers and (ii) biological systems.[183] It is notable that one can also envision creation of these versatile amide and heteroamide functionalities on nanotube sidewalls using either fluorinated or iodinated SWNTs as a precursor[184,185] and subsequently using these entities as building blocks in copolymerization and polycondensation reactions to create useful nanocomposite structures with enhanced physical properties.

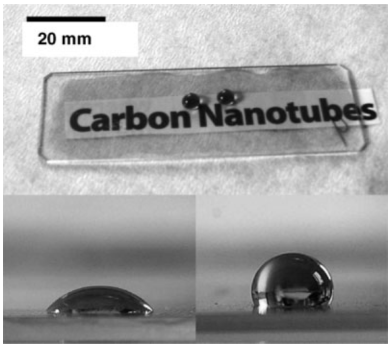


Figure 13. Top: an optically transparent, superhydrophobic PMMA composite film Bottom, left: side-view of a colored droplet on neat PMMA film. Bottom, right: side-view of the same droplet over the superhydrophobic composite film (diameter $<$ 2 mm). Reprinted with permission from [179]. Copyright 2008 American Chemical Society.

4.1. Covalently Functionalized Nanotube—Polymer Composites

It is widely recognized that the fabrication of high performance nanotube-polymer composites depends on an efficient load transfer from the host matrix to the nanotubes. To achieve the high loading of nanotubes requires the formation of a homogenous dispersion of nanotubes and strong interfacial bonding between the nanotubes and the polymer matrix.

Functionalized SWNTs covalently embedded into polymeric matrices tend to evince increased dispersibility as compared with their nonfunctionalized analogs.[186] For instance, a 1,3-dipolar cycloaddition reaction on the surface of SWNTs using octanal and 4-hydroxyphenyl glycine resulted in phenol-functionalized tubes that could be further derivatized with 2-bromoisobutyryl bromide, resulting in attachment of atom transfer radical polymerization initiators to the sidewalls of nanotubes; the resulting SWNTs, polymerized with methyl methacrylate and *t*-butyl acrylate, exhibited good solubility in a range of solvents, including aqueous ones.[187] Second, SWNTs that have been sidewall derivatized with polyethyleneimine[188] show enhanced solubility in aqueous media of up to 0.4 mg mL^{-1} and can absorb as much as 9.2% w/w of CO_2 at 27 °C. Third, poly(aminobenzene sulfonic acid) (PABS) and polyethylene glycol (PEG) covalently attached to SWNTs have yielded water-soluble graft copolymers[189] (Fig. 14) with solubilities approaching 5 mg mL^{-1}. Lastly, ''click chemistry'' has recently been employed as a mild and selective method to create SWNT–polymer composites with a high yield and full control over the resulting polymeric molecular weight. In this experiment, SWNTs were initially reacted with *p*-aminophenylpropargyl ether to produce alkyne-functionalized SWNTs that were then modified with a Cu(I)-catalyzed $(3+2)$ Huisgen cycloaddition to couple these nanomaterials with polystyrene polymers that had themselves been prepared by atom transfer radical polymerization. The resulting polymeric composites exhibited high solubility in THF, CH_2Cl_2, $CHCl_3$, as well as in other solvents (Figs. 15 and 16).[190]

Moreover, covalent binding of functionalized SWNTs onto polymeric surfaces can increase the degree of interfacial bonding or entanglement as compared with unfunctionalized SWNTs with improved mechanical properties.[186] For instance, nanotube-reinforced epoxy polymer composites have been prepared by covalently integrating SWNTs into the epoxy matrix. Upon mixing and reaction with functionalized SWNTs, containing pendant, terminal amino groups, a dramatic improvement in the mechanical properties of the resulting epoxy polymer material in terms of strength and modulus was noted.[191] Second, a series of 2.5, 5, 7.5, and 10 wt% SWNT/polypropylene composite fibers,[192] formed by a benzoyl peroxide initiated in situ functionalization of SWNTs, possesses improved mechanical properties in tensile strength of 82.9, 89.8, 72.3, and 173.1%, and in the elastic modulus of 69.2, 99.7, 137.2, and 133.7%, respectively, over that of neat polypropylene fibers. Third, fluorinated SWNTs covalently bound to a polypropylene matrix can noticeably improve mechanical properties (e.g., >100% increase in tensile modulus) with respect to pristine tubes.[193] Such an improvement in mechanical behavior is in agreement with theory.[194]

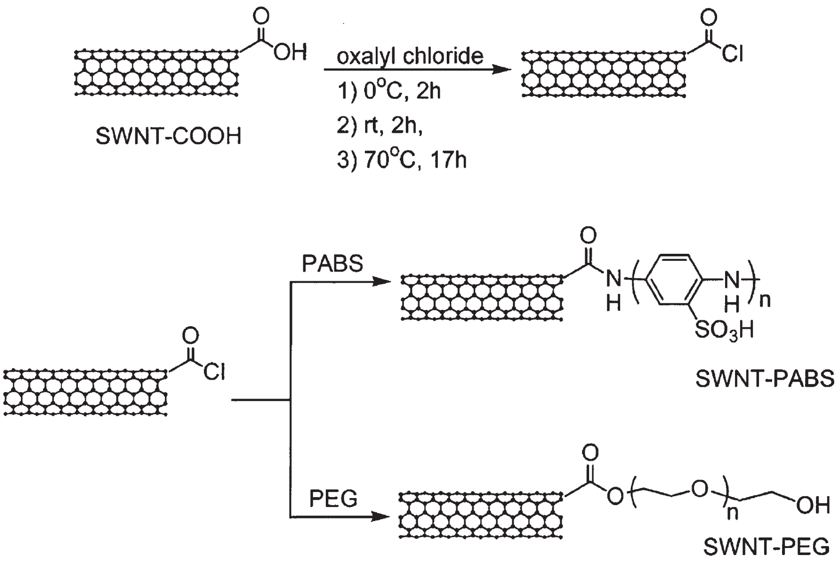


Figure 14. Synthesis of SWNT-PABS and SWNT-PEG graft copolymers. Reprinted with permission from [189]. Copyright 2005 American Chemical Society.

Recently, a "green" derivatization of SWNTs has been reported[195] in which amino groups on the SWNTs initiated polymerization into Nylon 6 in the presence of ε-caprolactam. Additional work [196] with in situ polymerization of caprolactam with SWNTs possessing carboxylic acid and amide functionalities showed that mechanical performance (e.g., Young's modulus) improved dramatically with a high concentration of carboxylic acid functional groups. A preponderance of amine groups on the SWNT surface increased the resulting nanocomposite's flexibility and toughness.

4.2. Biologically functionalized SWNT Platforms

The range of biologically relevant nanotube devices accessible through a myriad of covalent chemistry protocols we have discussed in this Report is astonishing.[197] Recently, SWNTs have been functionalized with DNA for gene delivery.[198] These results suggested that the interaction and electrostatic complex formation between ammonium-terminated SWNTs, prepared using azomethine ylide chemistry, and DNA was affected by both nanotube surface area and charge density. However, it was still unclear about the correlation between the degree of binding and gene expression efficiency.

Second, release of covalently attached biological cargo from nanotube sidewalls has been achieved through a cleavable disulfide linkage (Fig. 17). From confocal fluorescence images, fluorescence of Cy3-labeled DNA was observed within a mammalian cell nucleus upon release of the DNA from the SWNT surface after disulfide cleavage, whereas a control sample consisting of DNA–SWNT conjugates without a disulfide linkage accumulated in the perinuclear region. The same group also delivered siRNA into cells by using functionalized SWNTs, and noted a two-fold higher "silencing" efficiency as compared with using a commercial transfection agent, namely lipofectamine. This improvement was attributed to the high surface area of SWNTs for efficient siRNA cargo loading, the high intracellular transporting ability of SWNTs, and the high degree of endosome/lysosome escape ascribable to the reported disulfide approach.[199]

Third, elegant multimeric nanostructures incorporating SWNTs were constructed using a combination of programmed chemical reactions and molecular recognition.[200] Essentially, the device was based on an individual SWNT that was oxidatively cut by means of an oxygen plasma to yield carboxylic groups at the ends and then chemically "rewired" with a single conductive molecule (e.g., diaminofluorenone), which itself could "dock" with a target probe molecule. Hence, when the probe bound to its complementary biomolecule, it formed a noncovalent complex that could be reliably monitored at the single molecule level using electronic current measurements.

It is obvious that chemistry is being productively and imaginatively used to create highly useful composites and devices. Nonetheless, the complementary development of highly sensitive characterization techniques will be crucial to future advances in mechanistic understandings of all of the reactions we have described thus far. For instance, the Rice group has developed an elegant means of probing the absorption and emission spectra of individual nanotubes,[201] thereby providing evidence of a band gap-selective protonation of the sidewalls of the tubes, that was

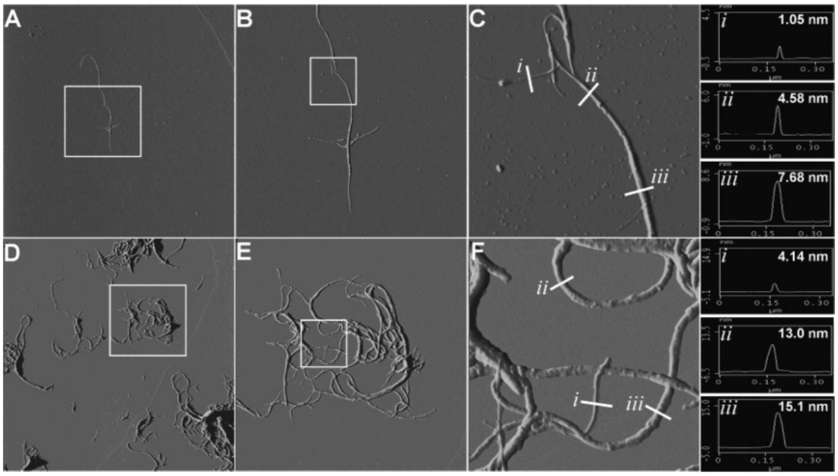


Figure 15. A–C) AFM images of pristine SWNTs and D, F) polystyrene-functionalized SWNTs, with height profiles of different sections of images C and F given on the right. Total scale bars of images vary from 15 μm (A and D) to 5 μm (B and E) and to 1 μm (C and F). Reprinted with permission from [190]. Copyright 2005 American Chemical Society.

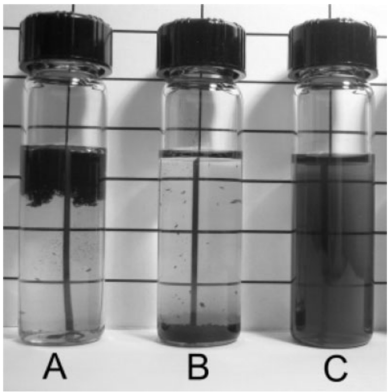


Figure 16. Photograph of three separate SWNT samples in THF. A) Pristine SWNTs; B) alkyne-functionalized SWNTs; and C) polymer-functionalized SWNTs. Reprinted with permission from [190]. Copyright 2005 American Chemical Society.

readily reversible by treatment with either base or UV light. They were later able to correlate spectrofluorimetric measurements[202] with Raman spectroscopy assignments[203] on individual carbon nanotubes and such an approach offers promise for characterizing individual functionalized SWNTs. Indeed, the same group has recently observed single-molecule chemical reactions with individual SWNTs using near-IR photoluminescence microscopy wherein the emission intensity within distinct submicron segments of individual SWNTs changed in discrete steps after exposure to acid, base, or diazonium reactants.[204]

The Collins group at UC Irvine has convincingly demonstrated the use of circuit conductance (Fig. 18) as a complementary means to monitor and control covalent attachment in situ to an electrically connected SWNT.[205] Specifically, discrete changes in the circuit conductance revealed chemical processes occurring in real time and allowed for bond formation and rupture at the SWNT sidewalls to be deterministically probed. Moreover, by electronically controlling electrochemical potentials, the same group could routinely measure single chemical attachments, including functionalization at one, two, or more discrete sites using three-terminal devices. Reactivity in the presence of sulfuric acid, e.g., through discrete oxidation and reduction events, was also investigated by exploiting device conductance.[206] Recently, the continuous interactions[207] (including subsequent hydrolysis) of a single carboxylate group, in the presence of EDC and a SWNT, were temporally analyzed over a period of hours through nuanced conductance changes; data were collected, in support of a mean active lifetime of 12 s for the carboxy–EDC complex. Overall, this was a broadly similar strategy to the selective electrochemical deposition process of nickel metal the same researchers had previously employed in identifying and counting highly reactive point defect sites on nanotube surfaces.[208] Spatially resolved tunneling spectroscopy as well as scanning gate microscopy have also been used to clarify the role of chemistry (specifically defects) on the transport properties of SWNTs, manipulated by local voltage pulses.[209,210]

We have recently used synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy as a particularly useful and effective technique for simultaneously probing the surface chemistry, surface molecular orientation, degree of order, and electronic structure of carbon nanotubes and related nanomaterials.[211–216] That is, we employed NEXAFS as an exciting, complementary tool to microscopy and spectroscopy for providing localized information about single-walled carbon nanotube and multi-walled carbon nanotube (MWNT) powders, films, and arrays as well as of boron nitride nanotubes. Specifically, for SWNTs and MWNTs, we analyzed their structure as a function of oxygenation/oxidation (e.g., comparison of wet-air oxidized, ozonized, and pristine tubes). In additional experiments, we compared the degree of order and alignment in nanotube powder, film, and aligned samples with those of graphite. For boron nitride nanotubes, we were able to identify phases of this material (e.g., hexagonal vs. cubic) and monitored the presence of defects and degree of crystallinity in nanoscale samples.

We foresee the development of additional characterization methodologies, including the use of sophisticated ultra-high vacuum techniques, that will be capable of providing multiple sources of information about structure and composition within a faster turnaround time. These advances will expand the flexibility and efficacy of directed chemical functionalization. The impor-

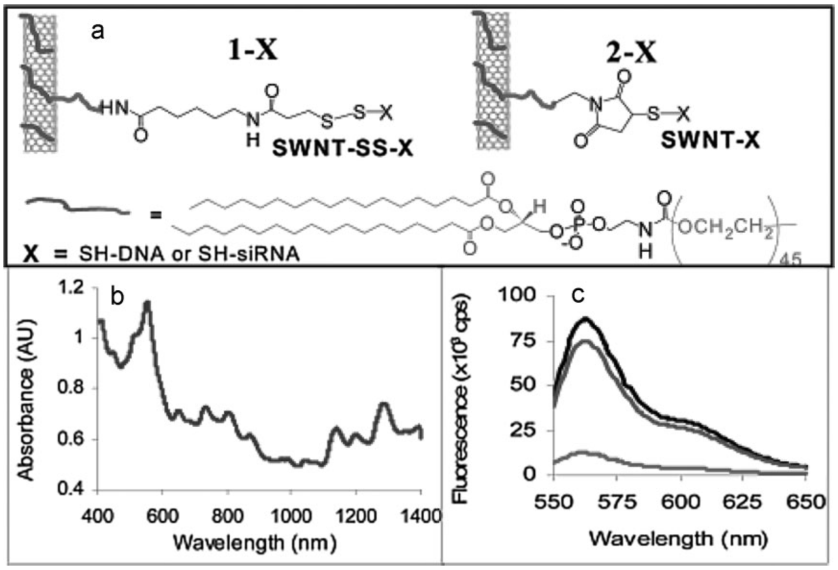


Figure 17. a) Two schemes of SWNT functionalization by thiolated biological molecule X with (**1**-X) and without (**2**-X) disulfide bond respectively. Both DNA and RNA cargoes contain a thiol functional group and a six-carbon long spacer at the 5′ end of the DNA or RNA. b) UV–Vis–near-IR of a **1**-DNA solution (peak at 550 nm due to Cy3 label on DNA) and c) fluorescence spectra (for Cy3 label) of a **1**-DNA and **2**-DNA, respectively, before (top) and after DTT (1,4-dithiothreitol)treatment and filtration (middle for **2**-DNA and bottom for **1**-DNA). Reprinted with permission from [199]. Copyright 2005 American Chemical Society.

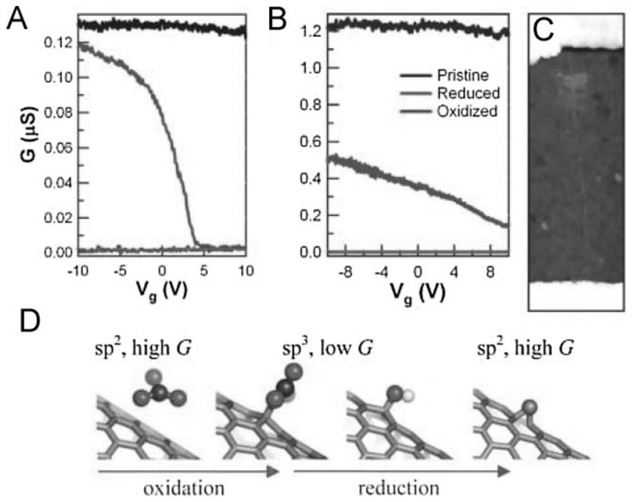


Figure 18. A, B) After a single redox cycle, metallic SWNTs show strong V_g dependences. G (V_g) is flat before oxidation (top), zero after oxidation (bottom), and then semiconductor-like after reduction (middle). Subsequent cycles have lesser effects on G, but flat G (V_g) curves were never recovered. It is also common for the G recovery to be incomplete in metallic SWNTs (B). C) A composite of AFM topography in grayscale and scanning gate microscopy in red identifies a local region responsible for the gate sensitivity of the device in (A). D) Proposed chemical process for HNO_3 oxidation and reduction, in which the redox cycle is not fully reversible but instead leaves behind a C–OH or C–O–C residue. The latter has sp^2 conjugation and restores the SWNT conductivity. Reprinted with permission from ref. [205]. Copyright 2007 American Association for the Advancement of Science.

tance of gaining an atomic level understanding of how structure and composition are precisely affected by chemical functionalization cannot be overemphasized.

Acknowledgements

We acknowledge the US Department of Energy (DE-AC02-98CH10886) for facility and personnel support. We also thank the National Science Foundation (CAREER award DMR-0348239), and the Alfred P. Sloan Foundation (2006–2008) for PI support and experimental supplies.

Received: May 29, 2008

---

[1] J. W. Mintmire, B. I. Dunlap, C. T. White, *Phys. Rev. Lett.* **1992**, *68*, 631.
[2] N. Hamada, S. Sawada, A. Oshiyama, *Phys. Rev. Lett.* **1992**, *68*, 1579.
[3] R. Saito, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *Phys. Rev. B* **1992**, *46*, 1804.
[4] R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Appl. Phys. Lett.* **1992**, *60*, 2204.
[5] C. T. White, D. H. Robertson, J. W. Mintmire, *Phys. Rev. B* **1993**, *47*, 5485.
[6] M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York **1996**.
[7] R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth, M. Kertesz, *Science* **1999**, *284*, 1340.
[8] R. H. Baughman, A. A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787.
[9] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, H. Dai, *Science* **1999**, *283*, 512.
[10] W. Zhao, C. H. Song, P. E. Pehrsson, *J. Am. Chem. Soc.* **2002**, *124*, 12418.
[11] J. Kong, M. G. Chapline, H. Dai, *Adv. Mater.* **2001**, *13*, 1384.
[12] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622.
[13] C.-M. Yang, K. Kaneko, M. Yudasaka, S. Iijima, *Nano Lett.* **2002**, *2*, 385.
[14] C.-M. Yang, H. Kanoh, K. Kaneko, M. Yudasaka, S. Iijima, *J. Phys. Chem. B* **2002**, *106*, 8994.
[15] A. Garg, S. B. Sinnott, *Chem. Phys. Lett.* **1998**, *295*, 273.
[16] S. C. Tsang, Y. K. Chen, P. J. F. Harris, M. L. H. Green, *Nature* **1994**, *372*, 159.
[17] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis, R. C. Haddon, *Acc. Chem. Res.* **2002**, *35*, 1105.
[18] M. A. Hamon, M. E. Itkis, S. Niyogi, T. Alvaraez, C. Kuper, M. Menon, R. C. Haddon, *J. Am. Chem. Soc.* **2001**, *123*, 11292.
[19] Z. Chen, W. Thiel, A. Hirsch, *ChemPhysChem.* **2003**, *4*, 93.
[20] J. Liu, A. G. Rinzler, H. J. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley, *Science* **1998**, *280*, 1253.
[21] M. N. Tchoul, W. T. Ford, G. Lolli, D. E. Resasco, S. Arepalli, *Chem. Mater.* **2007**, *19*, 5765.
[22] C. C. Wang, G. Zhou, J. Wu, B. L. Gu, W. H. Duan, *Appl. Phys. Lett.* **2006**, *89*, 173130.
[23] C. Wang, G. Zhou, H. Liu, J. Wu, Y. Qiu, B.-L. Gu, W. Duan, *J. Phys. Chem. B* **2006**, *110*, 10266.
[24] H. Yu, Y. Jin, Z. Li, F. Peng, H. Wang, *J. Solid State Chem.* **2008**, *181*, 432.
[25] S. Banerjee, S. S. Wong, *J. Phys. Chem. B* **2002**, *106*, 12144.
[26] S. Banerjee, S. S. Wong, *Nano Lett.* **2004**, *4*, 1445.
[27] Z. Y. Chen, R. H. Hauge, R. E. Smalley, *J. Nanosci. Nanotech.* **2006**, *6*, 1935.
[28] Z. Y. Chen, K. J. Ziegler, J. Shaver, R. H. Hauge, R. E. Smalley, *J. Phys. Chem. B* **2006**, *110*, 11624.
[29] T. Hemraj-Benny, T. J. Bandosz, S. S. Wong, *J. Coll. Interf. Sci.* **2008**, *317*, 375.
[30] L. C. Teague, S. Banerjee, S. S. Wong, C. A. Richter, B. Varughese, J. D. Batteas, *Chem. Phys. Lett.* **2007**, *442*, 354.
[31] S. Banerjee, T. Hemraj-Benny, S. S. Wong, *Adv. Mater.* **2005**, *17*, 17.
[32] U. Dettlaff-Weglikowska, V. Skakalova, R. Graupner, S. H. Jhang, B. H. Kim, H. J. Lee, L. Ley, Y. W. Park, S. Berber, D. Tomanek, S. Roth, *J. Am. Chem. Soc.* **2005**, *127*, 5125.
[33] L. Zhang, J. Zhang, N. Schmandt, J. Cratty, V. N. Khabashesku, K. F. Kelly, A. R. Barron, *Chem. Commun.* **2005**, 5429.
[34] M. S. Dresselhaus, G. Dresselhaus, P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Springer-Verlag, Berlin **2001**.
[35] J. L. Bahr, J. M. Tour, *J. Mater. Chem.* **2002**, *12*, 1952.
[36] M. E. Itkis, S. Niyogi, M. E. Meng, M. A. Hamon, H. Hu, R. C. Haddon, *Nano Lett.* **2002**, *2*, 155.
[37] D. Abdula, K. T. Nguyen, M. Shim, *J. Phys. Chem. C* **2007**, *111*, 17755.
[38] M. Dossot, F. Gardien, V. Mamane, Y. Fort, J. Liu, B. Vigolo, B. Humbert, E. McRae, *J. Phys. Chem. C* **2007**, *111*, 12199.
[39] Y. Lin, M. J. Meziani, Y.-P. Sun, *J. Mater. Chem.* **2007**, *17*, 1143.
[40] Y. Lin, B. Zhou, R. B. Martin, K. B. Henbest, B. A. Harruff, J. E. Riggs, Z. X. Guo, L. F. Allard, Y. P. Sun, *J. Phys. Chem. B* **2005**, *109*, 14779.
[41] D. M. Guldi, M. Holzinger, A. Hirsch, V. Georgakilas, M. Prato, *Chem. Commun.* **2003**, 1130.
[42] A. Jung, R. Graupner, L. Ley, A. Hirsch, *Phys. Stat. Sol. B* **2006**, *243*, 3217.
[43] J. Cabana, R. Martel, *J. Am. Chem. Soc.* **2007**, *129*, 2244.
[44] R. B. Martin, L. W. Qu, Y. Lin, B. A. Harruff, C. E. Bunker, J. R. Gord, L. F. Allard, Y. P. Sun, *J. Phys. Chem. B* **2004**, *108*, 11447.
[45] H. P. Li, M. E. Kose, L. W. Qu, Y. Lin, R. B. Martin, B. Zhou, B. A. Harruff, L. F. Allard, Y. P. Sun, *J. Photochem. Photobiol. A. Chem.* **2007**, *185*, 94.
[46] L. W. Qu, R. B. Martin, W. J. Huang, K. F. Fu, D. Zweifel, Y. Lin, Y.-P. Sun, *J. Chem. Phys.* **2002**, *117*, 8089.
[47] M. Alvaro, P. Atienzar, J. L. Bourdelande, H. Garcia, *Chem. Phys. Lett.* **2004**, *384*, 119.
[48] M. Alvaro, C. Aprile, B. Ferrer, H. Garcia, *J. Am. Chem. Soc.* **2007**, *129*, 5647.

[49] M. Alvaro, P. Atienzar, P. de la Cruz, J. L. Delgado, H. Garcia, F. Langa, *Chem. Phys. Lett.* **2004**, *386*, 342.

[50] W. H. Zhu, N. Minami, S. Kazaoui, Y. Kim, *J. Mater. Chem.* **2003**, *13*, 2196.

[51] M. Alvaro, C. Aprile, P. Atienzar, H. Garcia, *J. Phys. Chem. B* **2005**, *109*, 7692.

[52] A. Kongkanand, P. V. Kamat, *J. Phys. Chem. C* **2007**, *111*, 9012.

[53] M. A. Herranz, N. Martin, S. P. Campidelli, M. Prato, G. Brehm, D. M. Guldi, *Angew. Chem. Intl. Ed.* **2006**, *45*, 4478.

[54] C. Li, M. Curreli, H. Lin, B. Lei, F. N. Ishikawa, R. Datar, R. J. Cote, M. E. Thompson, C. W. Zhou, *J. Am. Chem. Soc.* **2005**, *127*, 12484.

[55] N. W. S. Kam, T. C. Jessop, P. A. Wender, H. J. Dai, *J. Am. Chem. Soc.* **2004**, *126*, 6850.

[56] K. V. Singh, R. R. Pandey, X. Wang, R. Lake, C. S. Ozkan, K. Wang, M. Ozkan, *Carbon* **2006**, *44*, 1730.

[57] N. T. Hu, G. D. Dang, H. W. Zhou, J. Jing, C. H. Chen, *Mater. Lett.* **2007**, *61*, 5285.

[58] S. Y. Ju, F. Papadimitrakopoulos, *J. Am. Chem. Soc.* **2008**, *130*, 655.

[59] S. Q. Wang, E. S. Humphreys, S.-Y. Chung, D. F. Delduco, S. R. Lustig, H. Wang, K. N. Parker, N. W. Rizzo, S. Subramoney, Y.-M. Chiang, A. Jagota, *Nat. Mater.* **2003**, *2*, 196.

[60] K. Y. Jiang, L. S. Schadler, R. W. Siegel, X. Zhang, H. Zhang, M. Terrones, *J. Mater. Chem.* **2004**, *14*, 37.

[61] W. Huang, S. Taylor, K. Fu, Y. Lin, D. Zhang, T. W. Hanks, A. M. Rao, Y.-P. Sun, *Nano Lett.* **2002**, *2*, 311.

[62] P. Asuri, S. S. Bale, R. C. Pangule, D. A. Shah, R. S. Kane, J. S. Dordick, *Langmuir* **2007**, *23*, 12318.

[63] Y. B. Zhang, M. Kanungo, A. J. Ho, P. Freimuth, D. van der Lelie, M. Chen, S. M. Khamis, S. S. Datta, A. T. C. Johnson, J. A. Misewich, S. S. Wong, *Nano Lett.* **2007**, *7*, 3086.

[64] X. Yu, B. Munge, V. Patel, G. Jensen, A. Bhirde, J. D. Gong, S. N. Kim, J. Gillespie, J. S. Gutkind, F. Papadimitrakopoulos, J. F. Rusling, *J. Am. Chem. Soc.* **2006**, *128*, 11199.

[65] B. C. Satishkumar, L. O. Brown, Y. Gao, C.-C. Wang, H.-L. Wang, S. K. Doorn, *Nat. Nanotechnol.* **2007**, *2*, 560.

[66] F. Nunzi, F. Mercuri, A. Sgamellotti, N. Re, *J. Phys. Chem. B* **2002**, *106*, 10622.

[67] R. C. Haddon, *Science* **1993**, *261*, 1545.

[68] S. Banerjee, S. S. Wong, *Nano Lett.* **2002**, *2*, 49.

[69] F. Mercuri, A. Sgamellotti, *J. Phys. Chem. B* **2006**, *110*, 15291.

[70] S. Banerjee, S. S. Wong, *J. Am. Chem. Soc.* **2002**, *124*, 8940.

[71] C. Baleizao, B. Gigante, H. Garcia, A. Corma, *J. Catal.* **2004**, *221*, 77.

[72] F. Frehill, J. G. Vos, S. Benrezzak, A. A. Koos, Z. Konya, M. G. Ruther, W. J. Blau, A. Fonseca, J. B. Nagy, L. P. Biro, A. I. Minett, M. in het Panhuis, *J. Am. Chem. Soc.* **2002**, *124*, 13694.

[73] H. Chaturvedi, J. C. Poler, *J. Phys. Chem. B* **2006**, *110*, 22387.

[74] R. F. Khairoutdinov, L. V. Doubova, R. C. Haddon, L. Saraf, *J. Phys. Chem. B* **2004**, *108*, 19976.

[75] T. Hemraj-Benny, S. Banerjee, S. S. Wong, *Chem. Mater.* **2004**, *16*, 1855.

[76] H. Ago, M. S. P. Shaffer, D. S. Ginger, A. H. Windle, R. H. Friend, *Phys. Rev. B* **2000**, *61*, 2286.

[77] L. Cao, H. Z. Chen, H. B. Zhou, L. Zhu, J. Z. Sun, X. B. Zhang, J. M. Xu, M. Wang, *Adv. Mater.* **2003**, *15*, 909.

[78] D. B. Romero, M. Carrard, W. De Heer, L. Zuppiroli, *Adv. Mater.* **1996**, *8*, 899.

[79] J. Duchet, B. Chabert, J. P. Chapel, J. F. Gerard, J. M. Chovelon, N. Jaffrezic-Renault, *Langmuir* **1997**, *13*, 2271.

[80] L. Valentini, J. Macan, I. Armentano, F. Mengoni, J. M. Kenny, *Carbon* **2006**, *44*, 2196.

[81] Y. J. Zhang, Y. F. Shen, D. X. Han, Z. J. Wang, J. X. Song, L. Niu, *J. Mater. Chem.* **2006**, *16*, 4592.

[82] T. Hemraj-Benny, S. S. Wong, *Chem. Mater.* **2006**, *18*, 4827.

[83] X. Lu, F. Tian, Q. Zhang, *J. Phys. Chem. B* **2003**, *107*, 8388.

[84] Y. Y. Chu, M. D. Su, *Chem. Phys. Lett.* **2004**, *394*, 231.

[85] C. Zhang, R. Li, Z. Shang, J. Li, Y. Xing, Y. Pan, Z. Cai, X. Zhao, *J. Mol. Struct. (Theochem.)* **2004**, *681*, 225.

[86] J. Lu, S. Nagase, X. Zhang, Y. Maeda, T. Wakahara, T. Nakahodo, T. Tsuchiya, T. Akasaka, D. Yu, Z. Gao, R. Han, H. Ye, *J. Mol. Struct. (Theochem.)* **2005**, *725*, 255.

[87] Y. Zhang, H. Dai, *Appl. Phys. Lett.* **2000**, *77*, 3015.

[88] R. Q. Yu, L. W. Chen, Q. P. Liu, J. Y. Lin, K.-L. Tan, S. C. Ng, H. S. O. Chan, G.-Q. Xu, T. S. A. Hor, *Chem. Mater.* **1998**, *10*, 718.

[89] Y. Zhang, N. W. Franklin, R. J. Chen, H. Dai, *Chem. Phys. Lett.* **2000**, *331*, 35.

[90] H. Mauser, A. Hirsch, N. J. R. van Eikema Hommes, T. Clark, *J. Mol. Model.* **1997**, *3*, 415.

[91] W. Zhang, T. M. Swager, *J. Am. Chem. Soc.* **2007**, *129*, 7714.

[92] A. Hirsch, *Angew. Chem. Intl. Ed.* **2002**, *41*, 1853.

[93] D. Tasis, N. Tagmatarchis, V. Georgakilas, M. Prato, *Chem. Eur. J.* **2003**, *9*, 4000.

[94] S. Niyogi, M. A. Hamon, H. Hu, B. Zhao, P. Bhowmik, R. Sen, M. E. Itkis, R. C. Haddon, *Acc. Chem. Res.* **2002**, *35*, 1105.

[95] M. Holzinger, J. Steinmetz, D. Samaille, M. Glerup, M. Paillet, P. Bernier, L. Ley, R. Graupner, *Carbon* **2004**, *42*, 941.

[96] M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss, F. Jellen, *Angew. Chem. Int. Ed.* **2001**, *40*, 4002.

[97] X. Lu, F. Tian, N. Wang, Q. Zhang, *Org. Lett.* **2002**, *4*, 4313.

[98] J. L. Delgado, P. de la Cruz, F. Langa, A. Urbina, J. Casado, J. T. Lopez Navarrete, *Chem. Commun.* **2004**, 1734.

[99] H. Hu, B. Zhao, M. A. Hamon, K. Kamaras, M. E. Itkis, R. C. Haddon, *J. Am. Chem. Soc.* **2003**, *125*, 14893.

[100] Y.-Y. Chu, M.-D. Su, *Chem. Phys. Lett.* **2004**, *394*, 231.

[101] X. Lu, F. Tian, Q. Zhang, *J. Phys. Chem. B* **2003**, *107*, 8388.

[102] K. S. Coleman, S. R. Bailey, S. Fogden, M. L. H. Green, *J. Am. Chem. Soc.* **2003**, *125*, 8722.

[103] M. Holzinger, J. Abraha, P. Whelan, R. Graupner, L. Ley, F. Hennrich, M. Kappes, A. Hirsch, *J. Am. Chem. Soc.* **2003**, *125*, 8566.

[104] X. Lu, F. Tian, X. Xu, N. Wang, Q. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 10459.

[105] Z. Chen, S. Nagase, A. Hirsch, R. C. Haddon, W. Thiel, P. v. R. Schleyer, *Angew. Chem. Int. Ed.* **2004**, *43*, 1552.

[106] Y. S. Lee, N. Marzari, *Phys. Rev. Lett.* **2006**, *97*, 116801.

[107] J. Lu, D. Wang, S. Nagase, M. Ni, X. W. Zhang, Y. Maeda, T. Wakahara, T. Nakahodo, T. Tsuchiya, T. Akasaka, Z. X. Gao, D. P. Yu, H. Q. Ye, Y. S. Zhou, W. N. Meit, *J. Phys. Chem. B* **2006**, *110*, 5655.

[108] J. M. Ashcroft, K. B. Hartman, Y. Mackeyev, C. Hofmann, S. Pheasant, L. B. Alemany, L. J. Wilson, *Nanotechnology* **2006**, *17*, 5033.

[109] T. Umeyama, N. Tezuka, M. Fujita, Y. Matano, N. Takeda, K. Murakoshi, K. Yoshida, S. Isoda, H. Imahori, *J. Phys. Chem. C* **2007**, *111*, 9734.

[110] V. N. Khabashesku, W. E. Billups, J. L. Margrave, *Acc. Chem. Res.* **2002**, *35*, 1087.

[111] L. Zhang, J. Z. Yang, C. L. Edwards, L. B. Alemany, V. N. Khabashesku, A. R. Barron, *Chem. Commun.* **2005**, 3265.

[112] V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger, A. Hirsch, *J. Am. Chem. Soc.* **2002**, *124*, 760.

[113] V. Georgakilas, D. Voulgaris, E. Vazquez, M. Prato, D. M. Guldi, A. Kukovecz, H. Kuzmany, *J. Am. Chem. Soc.* **2002**, *124*, 14318.

[114] F. G. Brunetti, M. A. Herrero, J. D. M. Munoz, S. Giordani, A. Diaz-Ortiz, S. Filippone, G. Ruaro, M. Meneghetti, M. Prato, E. Vazquez, *J. Am. Chem. Soc.* **2007**, *129*, 14580.

[115] J. Liu, M. R. I. Zubiri, B. Vigolo, M. Dossot, B. Humbert, Y. Fort, E. McRae, *J. Nanosci. Nanotechnol.* **2007**, *7*, 3519.

[116] J. X. Li, H. Grennberg, *Chem. Eur. J.* **2006**, *12*, 3869.

[117] V. Georgakilas, N. Tagmatarchis, D. Pantarotto, A. Bianco, J. P. Briand, M. Prato, *Chem. Commun.* **2002**, 3050.

[118] G. Pastorin, W. Wu, S. Wieckowski, J. P. Briand, K. Kostarelos, M. Prato, A. Bianco, *Chem. Commun.* **2006**, 1182.

[119] D. Pantarotto, C. D. Partidos, R. Graff, J. Hoebeke, J. P. Briand, M. Prato, A. Bianco, *J. Am. Chem. Soc.* **2003**, *125*, 6160.
[120] D. Pantarotto, C. D. Partidos, J. Hoebeke, F. Brown, E. Kramer, J. P. Briand, S. Muller, M. Prato, A. Bianco, *Chem. Biol.* **2003**, *10*, 961.
[121] D. Pantarotto, J. P. Briand, M. Prato, A. Bianco, *Chem. Commun.* **2004**, 16.
[122] J. H. Bae, A. M. Shanmugharaj, W. H. Noh, W. S. Choi, S. H. Ryu, *Appl. Surf. Sci.* **2007**, *253*, 4150.
[123] M. A. Herranz, C. Ehli, S. Campidelli, M. Gutierrez, G. L. Hug, K. Ohkubo, S. Fukuzumi, M. Prato, N. Martin, D. M. Guldi, *J. Am. Chem. Soc.* **2008**, *130*, 66.
[124] N. Tagmatarchis, M. Prato, D. M. Guldi, *Phys. E* **2005**, *29*, 546.
[125] M. Alvaro, P. Atienzar, P. de la Cruz, J. L. Delgado, H. Garcia, F. Langa, *J. Phys. Chem. B* **2004**, *108*, 12691.
[126] M. J. Gomez-Escalonilla, P. Atienzar, J. L. G. Fierro, H. Garcia, F. Langa, *J. Mater. Chem.* **2008**, *18*, 1592.
[127] S. Campidelli, C. Sooambar, E. L. Diz, C. Ehli, D. M. Guldi, M. Prato, *J. Am. Chem. Soc.* **2006**, *128*, 12544.
[128] B. Ballesteros, S. Campidelli, G. de la Torre, C. Ehli, D. M. Guldi, M. Prato, T. Torres, *Chem. Commun.* **2007**, 2950.
[129] B. Ballesteros, G. de la Torre, C. Ehli, G. M. A. Rahman, F. Agullo-Rueda, D. M. Guldi, T. Torres, *J. Am. Chem. Soc.* **2007**, *129*, 5061.
[130] C. Ehli, D. M. Guldi, M. A. Herranz, N. Martin, S. Campidelli, M. Prato, *J. Mater. Chem.* **2008**, *18*, 1498.
[131] J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, J. M. Tour, *J. Am. Chem. Soc.* **2001**, *123*, 6536.
[132] C. A. Dyke, M. P. Stewart, F. Maya, J. M. Tour, *Synlett.* **2004**, 155.
[133] J. L. Bahr, J. M. Tour, *Chem. Mater.* **2001**, *13*, 3823.
[134] C. A. Dyke, J. M. Tour, *Nano Lett.* **2003**, *3*, 1215.
[135] M. D. Ellison, P. J. Gasda, *J. Phys. Chem. C* **2008**, *112*, 738.
[136] C. Fantini, M. L. Usrey, M. S. Strano, *J. Phys. Chem. C* **2007**, *111*, 17941.
[137] C. A. Dyke, J. M. Tour, *J. Am. Chem. Soc.* **2003**, *125*, 1156.
[138] C. A. Dyke, J. M. Tour, *Chem. Eur. J.* **2004**, *10*, 813.
[139] M. S. Strano, *J. Am. Chem. Soc.* **2003**, *125*, 16148.
[140] J. L. Hudson, M. J. Casavant, J. M. Tour, *J. Am. Chem. Soc.* **2004**, *126*, 11158.
[141] J. J. Stephenson, J. L. Hudson, A. D. Leonard, B. K. Price, J. M. Tour, *Chem. Mater.* **2007**, *19*, 3491.
[142] J. J. Stephenson, J. L. Hudson, S. Azad, J. M. Tour, *Chem. Mater.* **2006**, *18*, 374.
[143] B. K. Price, J. M. Tour, *J. Am. Chem. Soc.* **2006**, *128*, 12899.
[144] J. L. Hudson, H. H. Jian, A. D. Leonard, J. J. Stephenson, J. M. Tour, *Chem. Mater.* **2006**, *18*, 2766.
[145] J. M. Tour, A. K. Flatt, B. Chen, *J. Phys. Chem. B* **2005**, *127*, 8918.
[146] A. K. Flatt, B. Chen, J. M. Tour, *J. Am. Chem. Soc.* **2005**, *127*, 8918.
[147] B. Chen, A. K. Flatt, H. H. Jian, J. L. Hudson, J. M. Tour, *Chem. Mater.* **2005**, *17*, 4832.
[148] B. K. Price, J. L. Hudson, J. M. Tour, *J. Am. Chem. Soc.* **2005**, *127*, 14867.
[149] C. D. Liang, J. F. Huang, Z. J. Li, H. M. Luo, S. Dai, *Eur. J. Org. Chem.* **2006**, 586.
[150] T. Fukushima, T. Aida, *Chem. Eur. J.* **2007**, *13*, 5048.
[151] Y. J. Zhang, Y. F. Shen, J. Li, L. Niu, S. Dong, A. Ivaska, *Langmuir* **2005**, *21*, 4797.
[152] P. G. Whitten, G. M. Spinks, G. G. Wallace, *Carbon* **2005**, *43*, 1891.
[153] F. Liang, A. K. Sadana, A. Peera, J. Chattopadhyay, Z. Gu, R. H. Hauge, W. E. Billups, *Nano Lett.* **2004**, *4*, 1257.
[154] J. Chattopadhyay, A. K. Sadana, F. Liang, J. M. Beach, Y. X. Xiao, R. H. Hauge, W. E. Billups, *Org. Lett.* **2005**, *7*, 4067.
[155] J. Chattopadhyay, S. Chakraborty, A. Mukherjee, R. Wang, P. S. Engel, W. E. Billups, *J. Phys. Chem. C* **2007**, *111*, 17928.
[156] F. Liang, L. B. Alemany, J. M. Beach, W. E. Billups, *J. Am. Chem. Soc.* **2005**, *127*, 13941.
[157] Y. Martinez-Rubi, J. Guan, S. Lin, C. Scriver, R. E. Sturgeon, B. Simard, *Chem. Commun.* **2007**, 5146.
[158] Y. Ying, R. K. Saini, F. Liang, A. K. Sadana, W. E. Billups, *Org. Lett.* **2003**, *5*, 1471.
[159] C. W. Padgett, D. W. Brenner, *Nano Lett.* **2004**, *4*, 1051.
[160] H. P. Peng, P. Reverdy, V. N. Khabashesku, J. L. Margrave, *Chem. Commun.* **2003**, 362.
[161] H. Q. Peng, L. B. Alemany, J. L. Margrave, V. N. Khabashesku, *J. Am. Chem. Soc* **2003**, *125*, 15174.
[162] J. Liu, M. R. I. Zubiri, M. Dossot, B. Vigolo, R. H. Hauge, Y. Fort, J. J. Ehrhardt, E. McRae, *Chem. Phys. Lett.* **2006**, *430*, 93.
[163] J. Liu, M. R. I. Zubiri, B. Vigolo, M. Dossot, Y. Fort, J. J. Ehrhardt, E. McRae, *Carbon* **2007**, *45*, 885.
[164] L. M. Wei, Y. F. Zhang, *Chem. Phys. Lett.* **2007**, *446*, 142.
[165] L. M. Wei, Y. F. Zhang, *Nanotechnology* **2007**, *18*, 495703.
[166] R. Graupner, J. Abraham, D. Wunderlich, A. Vencelova, P. Lauffer, J. Rohrl, M. Hundhausen, L. Ley, A. Hirsch, *J. Am. Chem. Soc.* **2006**, *128*, 6683.
[167] D. Wunderlich, F. Hauke, A. Hirsch, *Chem. Eur. J.* **2008**, *14*, 1607.
[168] M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. W. Shan, C. Kittrell, R. H. Hauge, J. M. Tour, R. E. Smalley, *Science* **2003**, *301*, 1519.
[169] S. Banerjee, S. S. Wong, *J. Am. Chem. Soc.* **2004**, *126*, 2073.
[170] P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, J. L. Margrave, R. E. Smalley, *Chem. Phys. Lett.* **1999**, *310*, 367.
[171] R. K. Saini, I. W. Chiang, H. P. Peng, R. E. Smalley, W. E. Billups, R. H. Hauge, J. L. Margrave, *J. Am. Chem. Soc.* **2003**, *125*, 3617.
[172] H. P. Peng, P. Reverdy, V. N. Khabashesku, J. L. Margrave, *Chem. Commun.* **2003**, 362.
[173] T. S. Balaban, M. C. Balaban, S. Malik, F. Hennrich, R. Fischer, H. Rosner, M. Kappes, *Adv. Mater.* **2006**, *18*, 2763.
[174] R. Barthos, D. Mehn, A. Demortier, N. Pierard, Y. Morciaux, G. Demortier, A. Fonseca, J. B. Nagy, *Carbon* **2005**, *43*, 321.
[175] Z. Liu, C. Davis, W. Cai, L. He, X. Chen, H. Dai, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 1410.
[176] H. Dumortier, S. Lacotte, G. Pastorin, R. Marega, W. Wu, D. Bonifazi, J.-P. Briand, M. Prato, S. Muller, A. Bianco, *Nano Lett.* **2006**, *6*, 1522.
[177] N. W. S. Kam, T. C. Jessop, P. A. Wender, H. Dai, *J. Am. Chem. Soc.* **2004**, *126*, 6850.
[178] C. M. Sayes, F. Liang, J. L. Hudson, J. Mendez, W. Guo, J. M. Beach, V. C. Moore, C. D. Doyle, J. L. West, W. E. Billups, K. D. Ausman, V. L. Colvin, *Toxicol. Lett.* **2006**, *161*, 135.
[179] V. Georgakilas, A. B. Bourlinos, R. Zboril, C. Trapalis, *Chem. Mater.* **2008**, *20*, 2884.
[180] P. W. Chiu, G. S. Duesberg, U. Dettlaff-Weglikowska, S. Roth, *Appl. Phys. Lett.* **2002**, *80*, 3811.
[181] N. O. V. Plank, R. Cheung, R. J. Andrews, *Appl. Phys. Lett.* **2004**, *85*, 3229.
[182] I. Vasiliev, S. A. Curran, *J. Appl. Phys.* **2007**, *102*, 024317.
[183] T. Ramanathan, F. T. Fisher, R. S. Ruoff, L. C. Brinson, *Chem. Mater.* **2005**, *17*, 1290.
[184] M. X. Pulikkathara, O. V. Kuznetsov, V. N. Khabashesku, *Chem. Mater.* **2008**, *20*, 2685.
[185] K. S. Coleman, A. K. Chakraborty, S. R. Bailey, J. Sloan, M. Alexander, *Chem. Mater.* **2007**, *19*, 1076.
[186] C. A. Dyke, J. M. Tour, *J. Phys. Chem. A* **2004**, *108*, 11151.
[187] Z. Yao, N. Braidy, G. A. Botton, A. Adronov, *J. Am. Chem. Soc.* **2003**, *125*, 16015.
[188] E. P. Dillon, C. A. Crouse, A. R. Barron, *ACS Nano* **2008**, *2*, 156.
[189] B. Zhao, H. Hu, A. Yu, D. Perea, R. C. Haddon, *J. Am. Chem. Soc.* **2005**, *127*, 8197.
[190] H. M. Li, F. O. Cheng, A. M. Duft, A. Adronov, *J. Am. Chem. Soc.* **2005**, *127*, 14518.
[191] J. Zhu, H. Q. Peng, F. Rodriguez-Macias, J. L. Margrave, V. N. Khabashesku, A. M. Imam, K. Lozano, E. V. Barrera, *Adv. Funct. Mater.* **2004**, *14*, 643.

[192] D. McIntosh, V. N. Khabashesku, E. V. Barrera, *J. Phys. Chem. C* **2007**, *111*, 1592.
[193] D. McIntosh, V. N. Khabashesku, E. V. Barrera, *Chem. Mater.* **2006**, *18*, 4561.
[194] S. Namilae, N. Chandra, C. Shet, *Chem. Phys. Lett.* **2004**, *387*, 247.
[195] V. A. Basiuk, C. Salvador-Morales, E. V. Basiuk, R. M. J. Jacobs, M. Ward, B. T. Chu, R. B. Sim, M. L. H. Green, *J. Mater. Chem.* **2006**, *16*, 4420.
[196] J. Gao, B. Zhao, M. E. Itkis, E. Bekyarova, H. Hu, V. Kranak, A. Yu, R. C. Haddon, *J. Am. Chem. Soc.* **2006**, *128*, 7492.
[197] A. Bianco, M. Prato, *Adv. Mater.* **2003**, *15*, 1765.
[198] R. Singh, D. Pantarotto, D. McCarthy, O. Chaloin, J. Hoebeke, C. D. Partidos, J. P. Briand, M. Prato, A. Bianco, K. Kostarelos, *J. Am. Chem. Soc.* **2005**, *127*, 4388.
[199] N. W. S. Kam, Z. Liu, H. J. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 12492.
[200] X. Guo, A. Whalley, J. E. Klare, L. Huang, S. O'Brien, M. Steigerwald, C. Nuckolls, *Nano Lett.* **2007**, *7*, 1119.
[201] M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science* **2002**, *297*, 593.
[202] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, R. B. Weisman, *Science* **2002**, *298*, 2361.
[203] M. S. Strano, S. K. Doorn, E. H. Haroz, C. Kittrell, R. H. Hauge, R. E. Smalley, *Nano Lett.* **2003**, *3*, 1091.
[204] L. Cognet, D. A. Tsyboulski, J.-D. R. Rocha, C. D. Doyle, J. M. Tour, R. B. Weisman, *Science* **2007**, *316*, 1465.
[205] B. R. Goldsmith, J. G. Coroneus, V. R. Khalap, A. A. Kane, G. A. Weiss, P. G. Collins, *Science* **2007**, *315*, 77.
[206] J. Mannik, B. R. Goldsmith, A. Kane, P. G. Collins, *Phys. Rev. Lett.* **2006**, *97*, 016601.
[207] B. R. Goldsmith, J. G. Coroneus, A. A. Kane, G. A. Weiss, P. G. Collins, *Nano Lett.* **2008**, *8*, 189.
[208] Y. Fan, B. R. Goldsmith, P. G. Collins, *Nature Mater.* **2005**, *4*, 906.
[209] M. Berthe, S. Yoshida, Y. Ebine, K. Kanazawa, A. Okada, A. Taninaka, O. Takeuchi, N. Fukui, H. Shinohara, S. Suzuki, K. Sumitomo, Y. Kobayashi, B. Grandidier, D. Stievenard, H. Shigekawa, *Nano Lett.* **2007**, *7*, 3623.
[210] J.-Y. Park, *Appl. Phys. Lett.* **2007**, *90*, 023112.
[211] S. Banerjee, T. Hemraj-Benny, M. Balasubramanian, D. A. Fischer, J. A. Misewich, S. S. Wong, *Chem. Commun.* **2004**, 772.
[212] S. Banerjee, T. Hemraj-Benny, M. Balasubramanian, D. A. Fischer, J. A. Misewich, S. S. Wong, *Chem. Phys. Chem.* **2004**, *5*, 1416.
[213] T. Hemraj-Benny, S. Banerjee, S. Sambasivan, M. Balasubramanian, D. A. Fischer, G. Eres, A. A. Puretzky, D. B. Geohegan, D. H. Lowndes, W. Han, J. A. Misewich, S. S. Wong, *Small* **2006**, *2*, 26.
[214] T. Hemraj-Benny, S. Banerjee, S. Sambasivan, D. A. Fischer, W. Han, J. A. Misewich, S. S. Wong, *PhysChemChemPhys.* **2005**, *7*, 1103.
[215] S. Banerjee, T. Hemraj-Benny, S. Sambasivan, D. A. Fischer, J. A. Misewich, S. S. Wong, *J. Phys. Chem. B* **2005**, *109*, 8489.
[216] T. Hemraj-Benny, S. Banerjee, S. Sambasivan, D. A. Fischer, G. Eres, A. A. Puretzky, D. B. Geohegan, D. H. Lowndes, J. A. Misewich, S. S. Wong, *Phys. Chem. Chem. Phys.* **2006**, *8*, 5038.