JOURNAL OF Materials CHEMISTRY
Feature Article

Covalent chemistry of single-wall carbon nanotubes

Jeffrey L. Bahr and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, Rice University MS222, Houston, Texas, 77005. E-mail: tour@rice.edu; Fax: +1 713-348-6250

Received 28th January 2002, Accepted 21st March 2002
First published as an Advance Article on the web 1st May 2002

Despite the extraordinary promise of single-wall carbon nanotubes, their realistic application in materials and devices has been hindered by processing and manipulation difficulties. Now that this unique material is readily available in near kilogram quantities (albeit still at high cost), research into means of chemical alteration is in full swing. The covalent attachment of appropriate moieties is anticipated to facilitate applications development by improving solubility and ease of dispersion, and providing for chemical attachment to surfaces and polymer matrices. While it is clear that more investigation is needed to elucidate the nature and locality of covalently attached moieties, developments to date indicate that carbon nanotubes may indeed be considered a true segment of organic chemistry. In this contribution, we review the current state of carbon nanotube covalent chemistry, and convey our anxious expectation that further developments will follow.

Introduction

Single-wall carbon nanotubes (SWNTs) are undoubtedly one of the more striking discoveries in the chemistry and materials genre in recent years. These unique structures possess tremendous strength,[1] an extreme aspect ratio, and are excellent thermal and electrical conductors.[2] A plethora of potential applications have been proposed, and some progress is being made towards commercial applications. It is however, apparent that chemical modification of SWNTs will be necessary for some applications. One can envision grafting of moieties that allow assembly of modified SWNTs onto surfaces for electronics applications, moieties that allow reaction with host matrices in composites, and sensing applications that may require the presence of a variety of functional groups bound to the SWNTs. There also of course exists the intrinsic scientific curiosity about what one may accomplish with these unique structures, analogous to studies of C_{60} shortly after its ready availability. A number of routes to non-covalent modification of SWNTs have been reported, including polymer wrapping and adsorption,[3–5] adsorption of amines[6] and molecules with large π-systems,[7] complexation with organometallic compounds,[8] and radio frequency glow-discharge plasma modification.[9] In this contribution, we focus on covalent approaches to chemical modification of carbon nanotubes. At first glance, judging from the number of reported reaction types (and the brevity of this review), the covalent chemistry of SWNTs is not particularly rich. Certainly, compared to the chemistry of C_{60}, about which hundreds if not thousands of papers have been written, this field is limited to date. Very recent developments in several labs, however, offer much hope for the further growth of this field.

Characterization of functionalized SWNTs

Before discussing the various methods of covalent functionalization that have been reported, we comment on characterization of the resulting materials. Specific applications of these techniques can be found in the works referenced throughout the subsequent sections. In our laboratory we have been at times distraught at our inability to declare success or failure in attempted functionalization reactions. In the words of Hirsch,[10] the characterization of products represent a constant problem in nanotube chemistry. A standard suite of techniques does not yet exist for adequate characterization of chemically modified SWNTs. Solution phase absorption spectroscopy is the most accessible technique that offers qualitative information about the electronic state of SWNTs, and hence functionalization. As seen in Fig. 1 (curve A), the absorption spectrum of pristine SWNTs (in this case SWNTs produced by the HiPco method)[11] contains a good deal of structure, referred to as the van Hove singularities. The bands centered at *ca.* 1400 nm and 800 nm are respectively attributed to the first and second singularities in semiconducting nanotubes, while the bands centered at *ca.* 500 nm (much less distinct) are attributed to the first transition in metallic tubes. The references in the sections that follow give ample evidence that significant modification of the nanotube sidewalls dramatically affects the solution phase UV/vis/NIR absorption spectra, leading to a complete loss of structure (see also Fig. 1). Traditional transmission Fourier transform infrared absorption spectroscopy (FTIR) is of marginal use in analysis due to the high molar absorptivity of SWNTs. However, Yates *et al.* have reported some success with specialized techniques.[12,13]

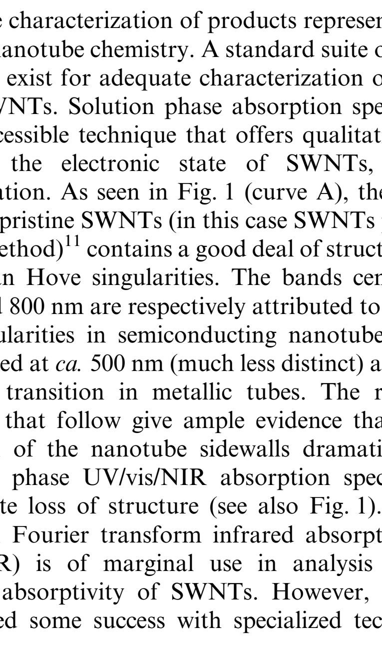

Fig. 1 Solution-phase absorption spectra in dimethylformamide, showing the complete loss of structure upon significant functionalization. A: pristine, unfunctionalized SWNTs produced by the HiPco process;[11] B: SWNTs functionalized with 4-bromophenyl moieties, by the electrochemical reduction of an aryl diazonium salt. This loss of structure is a consequence of the conversion of significant numbers of sp^2-hybridized carbons to sp^3-hybridization. Reproduced with permission from *J. Am. Chem. Soc.* 2001, **123**, 6536–6542. Copyright 2001 American Chemical Society.

DOI: 10.1039/b201013p

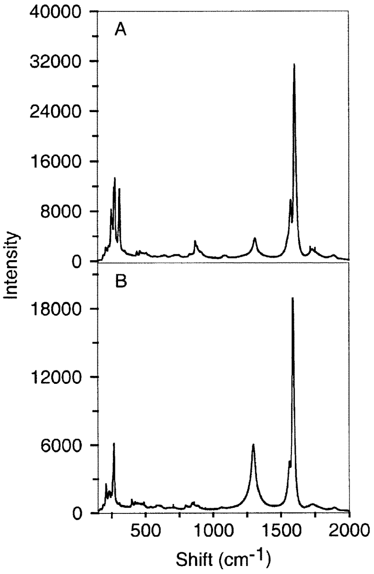

Fig. 2 Raman scattering spectra showing the increase in the relative intensity of the disorder mode (*ca.* 1290 cm^{-1}) upon significant functionalization, which is characteristic of the introduction of sp^3-hybridized carbons within the nanotube framework. A: pristine, unfunctionalized SWNTs; B: SWNTs functionalized with 4-carbomethoxyphenyl moieties, by the *in situ* generation and reaction of an aryl diazonium compound.

Attenuated-total-reflectance (ATR) accessories have allowed the general application of IR as a useful tool. Using this technique, characteristic absorption frequencies allow identification of functional groups bound to SWNTs. Both absorption and IR techniques are more difficult to employ in cases where functionalization is largely restricted to nanotube ends, as is the case with oxidizing acid and ozone treatments (*vide infra*). Nuclear magnetic resonance spectroscopy has found some application, although interpretation of the resulting spectra is difficult. Linewidths are typically quite broad due to a variety of factors, including residual paramagnetic material (SWNT growth catalysts), local field effects due to the nanotubes themselves, and slow tumbling of such large molecules in solution. Raman spectroscopy offers a great deal of useful information concerning functionalization of SWNTs, especially in cases of significant sidewall modification (see Fig. 2). SWNTs exhibit two main characteristic Raman modes: the diameter-dependent radial breathing (ω_r) mode, and the higher frequency tangential (ω_t) mode. Resonance enhancement furthers the utility of this technique. The radial breathing mode has found application in investigation of the relationship between tube diameter and reactivity. A third mode, the so-called disorder or sp^3 mode (found at *ca.* 1295 cm^{-1}) is diagnostic of disruptions in the hexagonal framework of the SWNTs. The relative intensity of this mode can then provide direct evidence of covalent modification. Thermal gravimetric analysis (TGA) gives useful insight into functionalized SWNTs, in particular because it has been shown that most functionalizing moieties are thermally labile. Coupling TGA with FTIR and mass spectroscopy can be expected to further enhance the usefulness of this technique. Microscopy techniques, including scanning electron (SEM), transmission electron (TEM), scanning-tunneling (STM) and atomic force (AFM) are powerful techniques that offer much insight. SEM and TEM images of pristine SWNTs are shown in Fig. 3. Although the resolution of these techniques is generally not sufficient to directly observe moieties attached by chemical modification moieties, perturbation of SWNT electronic structure can be probed, as well as functionalization effects on dispersion and exfoliation of ropes. Convincing evidence of covalent modification of SWNTs requires the corroborating application of many of the aforementioned techniques, in addition to elemental analysis by energy dispersive analysis with X-rays (EDAX) and X-ray photoelectron spectroscopy when unique signature providing elements are included.

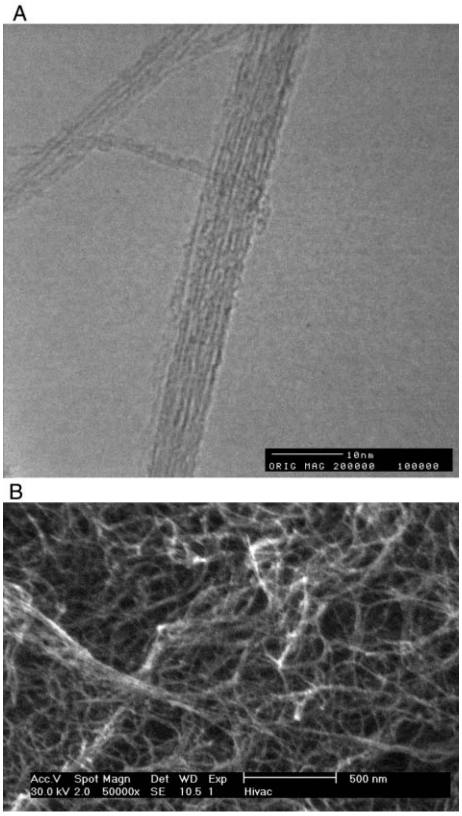

Fig. 3 A: TEM image of pristine SWNTs produced by the HiPco method; B: SEM image of HiPco SWNTs.[11]

Chemical modification of SWNTs

Oxidation and subsequent elaboration

The first reports of successful chemistry with SWNTs involved treatment under oxidizing conditions, such as sonication in mixtures of sulfuric and nitric acids, or treatment with piranha (sulfuric acid–hydrogen peroxide).[14,15] This type of treatment draws its inspiration from well known graphite chemistry.[16,17] In addition to cleaning of raw nanotube material by facilitating removal of amorphous and graphitic carbon (presumably made possible by differences in rate and extent of oxidation), these procedures cut (or 'etch') the SWNTs, as demonstrated by AFM determined length distributions. These cutting procedures leave the SWNTs open ended, the ends being decorated with a somewhat indeterminate number of oxygenated functionalities (see Fig. 4) such as carboxylic acids and anhydrides, quinones, and esters. Such functionalities can also be introduced by treatment of SWNTs with ozone.[12,13,18–20] The presence, plurality, and thermal removal of oxygenated functionalities generated by these methods have been investigated spectroscopically.[12,13] While the distribution of these functionalities has not been well characterized, they are presumed to exist primarily at the ends of nanotubes and at sites along the sidewalls where increased curvature strain results in increased reactivity.[21] The concept of higher reactivity at defect sites, or sites of increased curvature and partial loss of conjugation (especially end caps and kinks) has been touched upon by a number of authors,[21] as has the increased reactivity of smaller diameter SWNTs. Yates *et al.* showed that with *ca.* 1.4 nm diameter SWNTs, room temperature oxidation by ozone is confined to the end caps and the 'dangling' bonds created by the removal of these caps.[12] It

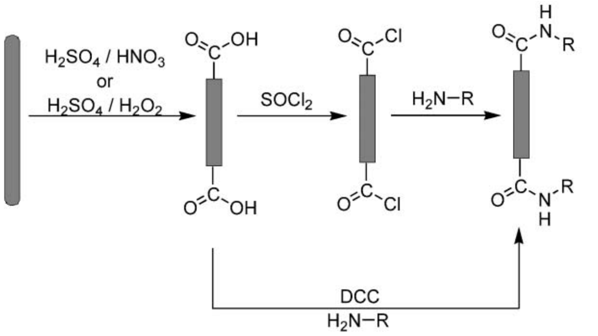

Fig. 4 Schematic depiction of oxidative etching of SWNTs followed by treatment with thionyl chloride, and subsequent amidation. The depiction here is for simplicity, and in deference to the difficulty in accurately determining the nature and location of oxygenated functionalities. It is understood that these oxidations also result in the introduction of moieties at defect sites along the sidewalls, and that functionalities other than carboxylic acids are formed (such as esters, quinones, and anhydrides). Additionally, although only one per end is shown, there are expected to be multiple functionalities at each end. Also shown is the dicyclohexylcarbodiimide coupling of a primary amine and SWNT carboxy groups. Alcohols have also been employed as the nucleophile, resulting in the formation of ester linkages.

was also shown that the functional groups created in this manner (primarily esters and quinones based on IR absorption frequencies) could be removed by heating in a vacuum to 600 °C, leaving the nanotube walls intact. In another study, Yates and Smalley employed a sort of 'ozone titration' to estimate that SWNTs produced by laser ablation of graphite targets, and purified by acidic oxidation, contained *ca.* 5% defect sites that were subject to facile oxidation.[13] A detailed study of diameter-dependent oxidative stability by Fischer *et al.*[22] has recently confirmed a direct relationship between diameter and reactivity. Using the resonance enhanced Raman radial breathing mode (a relationship of d (nm) = 224/(ω_r − 14)(cm^{-1}) has been developed for SWNTs within crystalline bundles),[23] the authors clearly showed that within a given sample of SWNTs, smaller diameter tubes are air oxidized more rapidly than larger diameter tubes. Further supporting the relationship between reactivity and curvature strain, preliminary experiments in our laboratory indicate that smaller diameter SWNTs (*ca.* 1 nm, produced by the HiPco process)[11] are more reactive towards ozone than larger diameter SWNTs produced by laser ablation of a graphite target.[15]

SWNTs oxidized by either acid or ozone treatment have been assembled on a number of surfaces, including silver,[24] highly-oriented-pyrolitic-graphite (HOPG),[25] and silicon.[26] High coverage densities and orientation normal to the surface have been shown, the latter being suggestive of higher degrees of functionalization at the nanotube ends. These ordered arrays of SWNTs may find use in a variety of applications, including field emission devices. We demonstrated the oxidation of HiPco SWNTs with UV/O_3, and the subsequent assembly of these SWNTs on rigid SAMs[20] (Fig. 5).

Exploitation of the functionalities introduced by these oxidative procedures through further chemical elaboration has taken many forms. Most obviously, the presence of carboxylic acid functionalities gives access to the vast field of peptide chemistry, and many reports have demonstrated elaboration *via* amide linkages. Most reported procedures involve initial treatment of the oxidized SWNTs with thionyl chloride for activation (Fig. 4), although carbodiimide couplings have also been reported. Smalley *et al.* demonstrated the attachment of gold nanoparticles subsequent to treatment of oxidized SWNTs with 11-aminoundecane-1-thiol.[14] Although the more nucleophilic thiol presumably results in the predominate formation of thioamides, free thiols were shown to exist *de facto* by AFM imaging of attached 10 nm gold nanoparticles. In a similar fashion, Liu *et al.* have assembled thiol derivatized SWNTs on gold substrates *via* a wet chemistry approach.[27] Lieber *et al.* have used end-functionalized SWNTs as probes for chemical force microscopy.[28] This technique offers the potential of true molecular resolution. Haddon *et al.* have reported the functionalization of oxidatively etched SWNTs with a number of moieties, including alkyl amines, and less nucleophilic aniline derivatives.[29,30] As in most other cases, the carboxylic acid bearing SWNTs were first treated with thionyl chloride for activation, as depicted in Fig. 4. In these functionalized materials, the SWNT ropes were reported to be largely exfoliated into individual nanotubes, in addition to having significantly increased solubility in organic solvents. This exfoliation of ropes is particularly important, as it facilitates manipulation and investigation of the spectroscopic properties of individual SWNTs. SWNTs solubilized in this manner were able to be purified by HPLC, offering functionalized material virtually free of contaminants.[31] It is understood that the chemical modes of attachment probably include imides (possibly from anhydrides) and other functionalities, and that these functionalities probably also exist along the SWNT sidewalls at, for example, oxidized defect sites; for simplicity and in deference to the difficulty of accurately ascertaining the true character, Fig. 4 depicts only the amide linkage at the oxidatively cut end of an SWNT. Haddon *et al.* also showed that simple acid–base chemistry is sufficient to improve the solubility of SWNTs in organic solvents.[29,32] Sun *et al.* have attached both lipophilic and hydrophilic dendron type species *via* amide and ester linkages,[33] and showed that these groups can be removed under basic or acidic hydrolysis conditions.[34] The defunctionalization reactions provide additional evidence for the nature of the attachment. Polymer

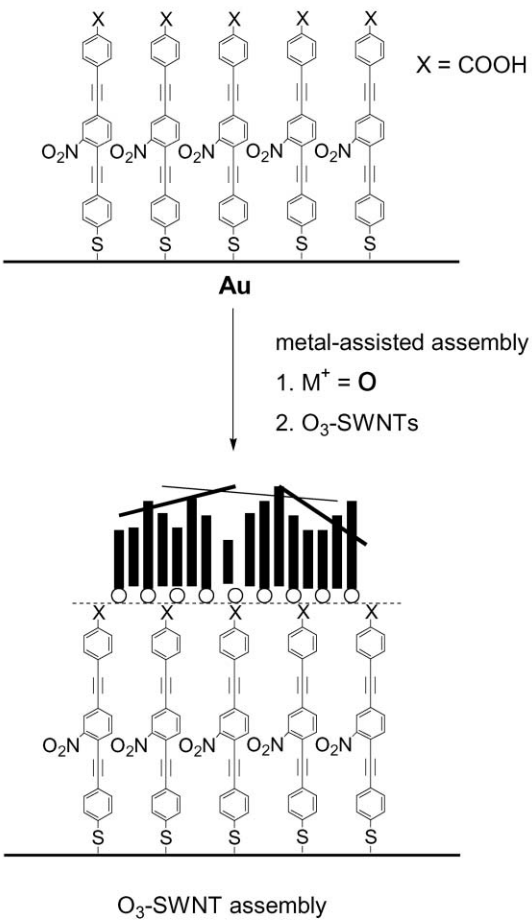

Fig. 5 Depiction of ozonation of HiPco SWNTs and subsequent deposition on a rigid SAM terminated with Fe^{3+} bound to the carboxylic groups of the SAM.[20]

chains have also been attached to oxidized SWNTs.[35,36] Sun *et al.* covalently attached a poly(propionylethylenimine-*co*-ethylenimine) polymer by both amidation of the acyl chloride form of oxidized SWNTs and by carbodiimide coupling. These polymer bound SWNTs were soluble in organic solvents, enabling investigation of the fluorescence properties. Finally, a theoretical study by Basiuk *et al.* found that a significant energetic difference between amidation of carboxylic groups in armchair and zigzag SWNTs exists.[37] Experimental verification of this prediction might enable selective solubilization, and hence separation, of different SWNT types.

It has been pointed out that the types of modifications discussed in the above paragraphs, being primarily restricted to nanotube ends, are too localized to appreciably change the bulk properties of the material. Attesting to this fact, these functionalizations do not significantly affect the spectroscopic properties of the SWNTs, as is seen in more extensive sidewall functionalizations (*vide infra*). For some applications, however, this type of localized chemistry may be desirable, as the full electronic capabilities of the SWNTs remain intact. Despite the localized nature of this chemistry, the solubility of the resulting SWNTs is generally improved. Unfortunately, there is little evidence for more elaborate comparisons among the different materials discussed above, the electronic and other effects on the SWNTs being largely the same.

Fluorination

The first report of extensive sidewall functionalization of SWNTs, fluorination, was made by Margrave *et al.* in 1998.[38] Employing a bucky paper (formed by filtration of an SWNT suspension over a PTFE membrane), and temperatures ranging from 150 °C to 600 °C, the authors were able, in some cases, to achieve a stoichiometry of up to C_2F, using elemental fluorine as the fluorinating agent (Fig. 6). At temperatures of 400 °C and higher, most of the SWNT structure was apparently destroyed. As expected, the successfully fluorinated material exhibited significant changes in the spectroscopic properties (UV/Vis/NIR absorption and Raman scattering), providing evidence for electronic perturbation that was not found in the earlier oxidized materials, owing to the predominately end-cap locale of the functionalizations (*vide supra*). In addition, the electrical conductivity of the functionalized material differed dramatically from the pristine SWNTs: a sample of untreated SWNTs was reported to have a resistance of 10–15 Ω, while a fluorinated SWNT sample had a resistance of > 20 MΩ (two probe measurement, similar sample size and thickness). Fluorinated SWNTs were found to be appreciably soluble in alcoholic solvents, and evidence was shown for exfoliation of ropes and bundles into individual nanotubes.[39] Recent theoretical investigations of fluorinated SWNTs by Bettinger *et al.*[40] indicate that while the thermodynamic stability of fluorinated SWNTs decreases with tube diameter, the mean bond dissociation energy for the C–F bonds increases as the diameter decreases. The C–F bonds were also found to be covalent in nature (1.41 to 1.45 Å in length). While not yet verified experimentally, it was predicted that endohedral fluorination of (5,5) SWNTs is thermodynamically possible. Margrave *et al.* have also shown that the majority of the covalently bound fluorine could be removed by treatment with hydrazine (Fig. 6), restoring much of the conductivity and spectroscopic properties of the pristine material. It was later shown that fluorine substituents on SWNTs can be displaced by treatment with strong nucleophiles such as Grignard and alkyllithium reagents, and metal alkoxides.[39,41] These reactions are thought to proceed *via* a concerted, allylic displacement mechanism, as back-side (S_N2) attack is not possible, and the stability of a cationic intermediate (S_N1 mechanism) is questionable. Extension of this displacement capability to functional group-tolerant reagents will further the utility of this chemistry. Fluorinated SWNTs have been employed as cathodes in lithium electrochemical cells, and are expected to be useful in other applications.[42]

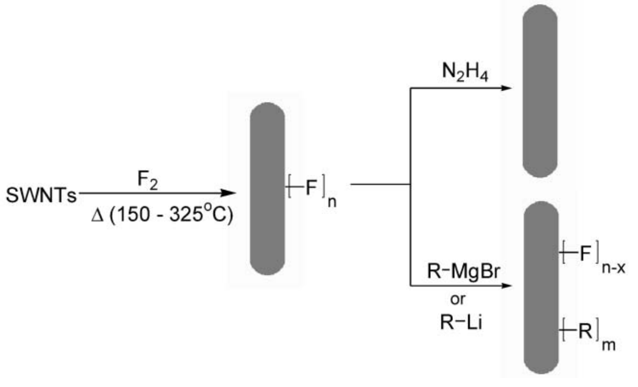

Fig. 6 Depiction of fluorination of SWNTs by Margrave *et al.*[38,39] A stoichiometry of up to C_2F can be achieved. Also shown are reductive defluorination with hydrazine, and displacement of fluorines with strong nucleophiles.[39,41]

Aryl diazonium chemistry

After initial efforts in our laboratory to further the chemistry of oxidatively etched SWNTs produced by laser ablation, we were quite thrilled to obtain a quantity of HiPco produced SWNTs[22] possessing significantly smaller diameters on average. The anticipated greater reactivity of these smaller diameter engendered hopes of successful functionalization with a variety of chemistries. During the course of our investigations, we have developed the reactivity of SWNTs with aryl diazonium compounds.[43,44] The reactivity of aryl diazonium salts with HOPG and other carbon surfaces has been previously demonstrated.[45] We first reported the use of a bucky paper electrode in an electrochemical reaction, as shown in Fig. 7.[43] Using this technique, we prepared a variety of functionalized SWNT materials. This reaction presumably proceeds *via* the aryl radical generated upon one electron reduction of the diazonium salt. This degree of functionalization is sufficient to cause a complete loss of structure in the solution-phase

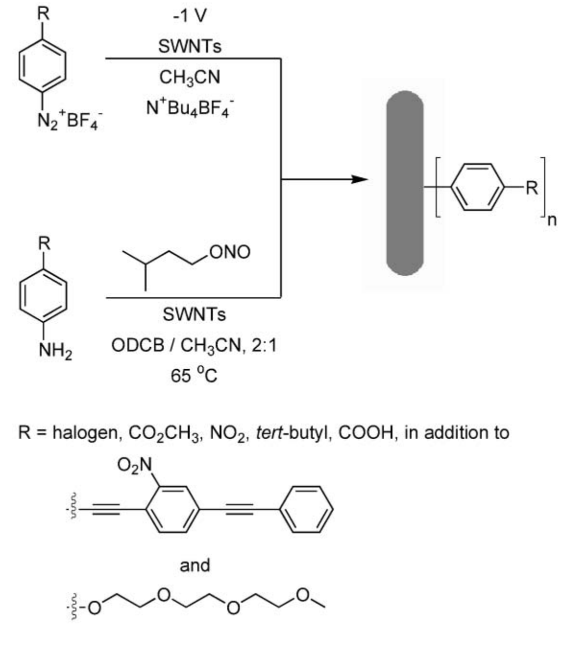

Fig. 7 Reaction of SWNTs with aryl diazonium compounds.[43,44] Shown are the electrochemical reaction with pre-formed diazonium salts, and the thermally motivated reaction with *in-situ* generated diazonium compounds. Also shown are a number of specific moieties that have been attached *via* these methods.

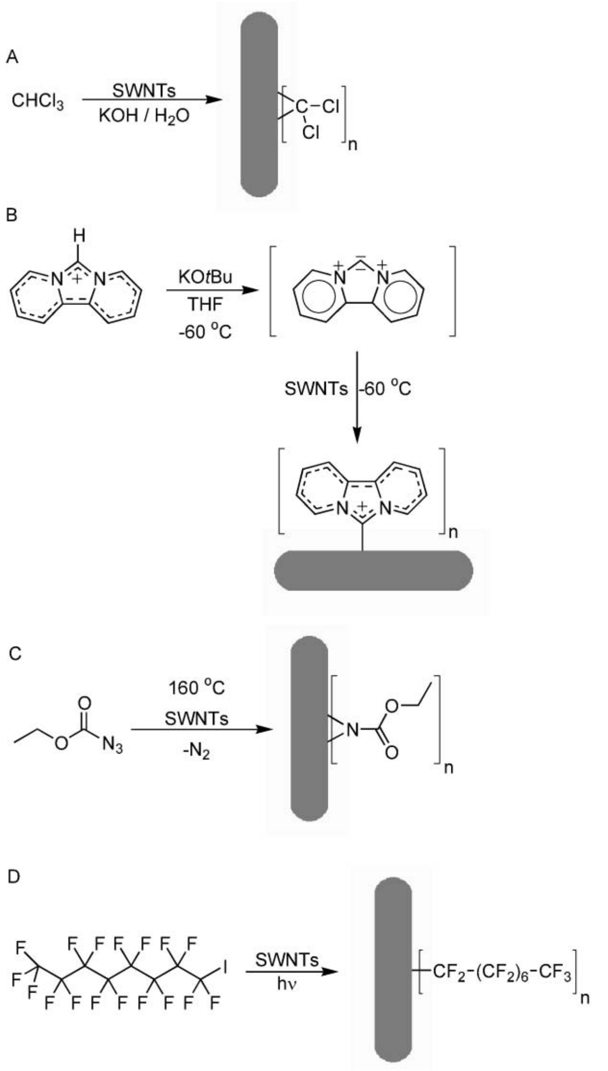

Fig. 8 Schematic depiction of a number of SWNT functionalization techniques. A: dichlorocarbene generated by base treatment of chloroform;[21] B: a nucleophilic carbene functionalization;[10] C: functionalization with nitrenes generated by thermolysis of an alkyl azidoformate;[10] D: reaction with radicals photolytically generated from a perfluoroalkyl iodide.[10]

absorption spectra, as shown in Fig. 1. Changes are observed in the Raman spectra as well, most notably a significant increase in the relative intensity of the disorder mode at *ca.* 1290 cm^{-1} (Fig. 2). These changes are reminiscent of the effect of fluorination (*vide supra*), and are consistent with sidewall as well as endcap functionalization. Based on thermal gravimetric and elemental analysis, we were able to achieve functionalization of 1 in 40 up to 1 in 20 nanotube carbons, using aryl diazonium salts bearing a variety of substituents. Some of the materials we prepared did not exhibit dramatic changes in solubility, and AFM analysis did not indicate significant exfoliation of SWNT ropes. The most logical explanation for the insignificant exfoliation draws on the fact that the SWNTs obviously exist as large ropes in the bucky-paper form employed for the reaction, and the conditions might not allow significant intercalation in these structures. Further investigation of the distribution of moieties, perhaps by STM, is required. We later described a similar reaction utilizing *in-situ* generation of the diazonium from the aniline precursor (Fig. 7).[44] This technique was found to be similar to the electrochemical method in its effectiveness, and avoids the necessity of isolating and storing diazonium salts that could be unstable. This method is also more traditional in nature, and offers the prospect of facile scale-up. We have in fact performed this type of reaction on a gram (SWNTs) scale.

Carbenes, nitrenes, and radicals

Haddon *et al.* have reported functionalization of SWNTs with dichlorocarbene, first generated from chloroform in the traditional manner with potassium hydroxide (Fig. 8A),[21] and later from phenyl(bromodichloromethyl)mercury.[30] Such carbenes are well known electrophilic reagents that can add to carbon–carbon double bonds. However, the degree of functionalization in these cases was low. Hirsch *et al.* have recently reported functionalization of SWNTs with the nucleophilic carbene shown in Fig. 8B, generated by deprotonation of the stable imidizolinium cation.[10] One negative charge per attached moiety is transferred to the nanotube by this reaction. Similarly, functionalization by nitrenes generated by thermolysis of alkyl azidoformates was reported (Fig. 8C). Evidence for these functionalizations was obtained from AFM and ^1H and ^{19}F NMR, in addition to solubility changes. Again, the degree of functionalization in these reactions was not sufficient to significantly affect the absorption spectra of the resulting materials relative to pristine SWNTs. Further investigation is needed to quantify the degree of functionalization, and to determine the distribution of moieties. Consistent with the observations of other groups, the authors also noted an apparent greater reactivity of smaller diameter arc-discharge SWNTs *versus* larger diameter laser ablation material. Functionalization of SWNTs utilizing radical sources other than aryl diazoniums has also been reported, including benzophenone[21] and perfluoroalkyl iodides (Fig. 8D).[10]

Azomethine ylides

Prato *et al.* have very recently discovered a method of functionalizing SWNTs utilizing 1,3-dipolar addition of azomethine ylides (Fig. 9).[46] This type of chemistry was originally developed for, and has seen wide-spread use in, C_{60} modification.[47,48] Thus, treatment of SWNTs suspended in DMF with an aldehyde and an *N*-substituted glycine derivative, at 130 °C, resulted in the formation of substituted pyrrolidine moieties on the SWNT surface. The technique was reported to be successful with both native and oxidatively etched SWNTs, and with SWNTs prepared by several different methods (and hence of different diameter distributions). In the case of pyrene containing moieties (Fig. 9(d)), the degree of

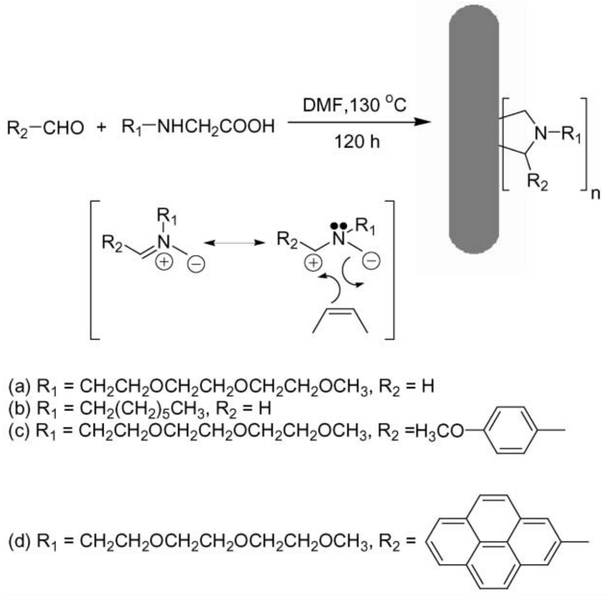

Fig. 9 Functionalization of SWNTs by the 1,3-dipolar addition of azomethine ylides.[45] Originally developed for C_{60} modification, this technique also offers the benefit of generality in chemical modification of SWNTs.

functionalization was estimated to be 1 in 95 nanotube carbons. Of particular note is the fact that sonication was strictly avoided throughout the reported experiments. Since a portion of the resulting materials was quite soluble in both organic solvents and water (*ca.* 50 mg mL^{-1} in chloroform for Fig. 9(a)), it seems likely that some exfoliation of ropes occurs during the course of the reaction, exposing new SWNT surface for modification. The ability to avoid sonication may be important for applications that require full-length SWNTs, such as some composite materials (re. sonication is known to affect SWNTs length distributions). The authors also note an effect on the NIR absorption spectrum, consistent with the loss of structure upon functionalization that we have observed in our laboratory.

Reduction

Several methods for dissolved metal reduction of SWNTs have been described. Haddon *et al.* first reported the Birch reduction of SWNTs by lithium in 1,2-diaminoethane.[21] This report was followed several years later by an extensive report on hydrogenation of SWNTs using lithium in liquid ammonia by Pekker *et al.*[49] Through an elegant series of TG-MS investigations, an approximate C : H ratio of 10.6 : 1 was obtained. The hydrogen thus bound to the SWNTs is not released until *ca.* 500 °C, indicating robust attachment. Also of considerable interest, the authors directly compared the reactivity of SWNTs to that of turbostratic graphite flakes and graphite powder. The estimated C : H ratios for these materials were, for graphite powder, 5.5 : 1, and for turbostratic graphite flakes, 4.5 : 1 (compare to 10.6 : 1 for SWNTs, *vide supra*). The more extensive hydrogenation of the graphitic materials does not by itself indicate a generalized higher reactivity for these materials, but the comparison is noteworthy.

Conclusions

While the number of reaction types reported to date is not extensive, particularly compared to the chemistry of C_{60} and other fullerenes, there now exist methods for chemical modification of both the sidewalls and ends of both native and oxidatively etched SWNTs. Due to the difficult nature of characterization, further investigation of the resulting materials is necessary, in particular to determine the distribution of moieties if possible, and to obtain more accurate estimates of the degree of functionalization. It is noteworthy that several of the major reaction types available for modification of SWNTs (oxidation, fluorination, and aryl diazonium chemistry) originate in the chemistry of HOPG, glassy carbon, or graphite. Only one direct comparison of the reactivity of SWNTs to other carbonaceous materials is available, (the dissolved metal reduction, *vide supra*) and is likely not the best generalization of reactivity. Of further hindrance to reactivity comparison is that reaction failures are often not reported in the literature. We thus cannot ascertain whether other chemistries are unsuccessful or simply have not been investigated, although in our laboratory we have investigated numerous reaction conditions and found limited success. In light of characterization difficulties, we concede that some of these attempted reactions may have been successful, but simply fell beneath our 'modification radar'. It is promising that, consistent with theoretical predictions, a number of authors have noted that smaller diameter SWNTs exhibit a greater reactivity. This bodes well for further development of SWNT chemistry, particularly employing the smaller diameter SWNTs synthesized by the HiPco technique that is projected to soon produce multi-kilogram quantities.[50] We anticipate the utilization of functionalized SWNTs in composites, and other applications where the robust attachment of moieties may offer significant benefit. In particular, the generality of the aryl diazonium chemistry developed in our laboratory,[43,44] and the 1,3-dipolar addition technique developed by Prato *et al.*[48] may be especially well suited to rational design of materials. We, and no doubt others, remain invigorated in our quest.

Acknowledgement

Research performed in our laboratory has been financially supported by NASA, NSF, and DARPA/ONR. We gratefully acknowledge the experimental contributions of our colleagues, who are named in the references.

References

1 M.-F. Yu, B. S. Files, S. Arepalli and R. S. Ruoff, *Phys. Rev. Lett.*, 2000, **84**, 5552.

2 R. Saito, G. Dresselhaus and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.

3 M. J. O'Connell, P. J. Boul, L. M. Ericson, C. B. Huffman, Y. Huang, E. H. Haroz, K. D. Ausman and R. E. Smalley, *Chem. Phys. Lett.*, 2001, **342**, 265–271.

4 A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S.-W. Chung, H. Choi and J. R. Heath, *Angew. Chem.*, 2001, **113**, 1721–1725.

5 M. Shim, A. Javey, N. Wong, S. Kam and H. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 11512–11513.

6 J. Kong and H. Dai, *J. Phys. Chem. B*, 2001, **105**, 2890–2893.

7 R. J. Chen, Y. Zhang, D. Wang and H. Dai, *J. Am. Chem. Soc.*, 2001, **123**, 3838–3839.

8 S. Banerjee and S. S. Wong, *NanoLetters*, 2001, **1**.

9 Q. Chen, L. Dai, M. Gao, S. Huang and A. Mau, *J. Phys. Chem. B*, 2001, **105**, 618–622.

10 M. Holzinger, O. Vostrowsky, A. Hirsch, F. Hennrich, M. Kappes, R. Weiss and F. Jellen, *Angew. Chem., Int. Ed.*, 2001, **40**, 4002–4005.

11 P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith and R. E. Smalley, *Chem. Phys. Lett.*, 1999, **313**, 91–97.

12 D. B. Mawhinney, V. Naumenko, A. Kuznetsova and J. T. Yates, Jr., *J. Am. Chem. Soc.*, 2000, **122**, 2383–2384.

13 D. B. Mawhinney, V. Naumenko, A. Kuznetsova, J. T. Yates, Jr., J. Liu and R. E. Smalley, *Chem. Phys. Lett.*, 2000, **324**, 213–216.

14 J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Macias-Rodriguez, Y.-S. Shon, T. R. Lee, D. T. Colbert and R. E. Smalley, *Science*, 1998, **280**, 1253–1256.

15 A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. Rodriguez-Macias, P. J. Boul, A. H. Lu, D. Heymann, D. T. Colbert, R. S. Lee, J. E. Fischer, A. M. Rao, P. C. Eklund and R. E. Smalley, *Appl. Phys. A*, 1998, **67**, 29–37.

16 K. Kinoshita, *Carbon Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.

17 S. F. McKay, *J. Appl. Phys.*, 1992, **35**, 1992.

18 A. Kuznetsova, I. Popova, J. T. Yates, M. J. Bronikowski, C. B. Huffman, J. Liu, R. E. Smalley, H. H. Hwu and J. G. Chen, Jr., *J. Am. Chem. Soc.*, 2001.

19 J. P. Deng, C. Y. Mou and C. C. Han, *Fullerene Science and Technology*, 1997, **5**, 1033.

20 L. Cai, J. L. Bahr, Y. Yao and J. M. Tour, submitted.

21 Y. Chen, R. C. Haddon, S. Fang, A. M. Rao, P. C. Eklund, W. H. Lee, E. C. Dickey, E. A. Grulke, J. C. Pendergrass, A. Chavan, B. E. Haley and R. E. Smalley, *J. Mater. Res.*, 1998, **13**, 2423–2431.

22 W. Zhou, Y. H. Ooi, R. Russo, P. Papanek, D. E. Luzzi, J. E. Fischer, M. J. Bronikowski, P. A. Willis and R. E. Smalley, *Chem. Phys. Lett.*, 2001, **350**, 6–14.

23 A. M. Rao, J. Chen, E. Richter, U. Schlecht, P. C. Eklund, R. C. Haddon, U. D. Venkateswaran, Y. K. Kwon and D. Tomanek, *Phys. Rev. Lett.*, 2001, **86**.

24 B. Wu, J. Zhang, Z. Wei, S. Cai and Z. Liu, *J. Phys. Chem. B*, 2001, **105**, 5075–5078.

25 H. Yanagi, E. Sawada, A. manivannan and L. A. Nagahara, *Appl. Phys. Lett.*, 2001, **78**, 1355–1357.

26 D. Chattopadhyay, I. Galeska and F. Papadimitrakopoulos, *J. Am. Chem. Soc.*, 2001, **123**, 9451–9452.

27 Z. Liu, Z. Shen, T. Zhu, S. Hou and L. Ying, *Langmuir*, 2000, **16**, 3569–3573.

28 S. S. Wong, A. T. Woolley, E. Joselevich, C. L. Cheung and C. M. Lieber, *J. Am. Chem. Soc.*, 1998, **120**, 8557–8558.

29 M. A. Hamon, J. Chen, H. Hu, Y. Chen, M. E. Itkis, A. M. Rao, P. C. Eklund and R. C. Haddon, *Adv. Mater.*, 1999, **11**, 834–840.

30 J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund and R. C. Haddon, *Science*, 1998, **282**, 95–98.

31 B. Zhao, H. Hu, S. Niyogi, M. E. Itkis, M. A. Hamon, P. Bhowmik, M. S. Meier and R. C. Haddon, *J. Am. Chem. Soc.*, 2001, **123**, 11673–11677.

32 J. Chen, A. M. Rao, S. Lyuksyutov, M. E. Itkis, M. A. Hamon, H. Hu, R. W. Cohn, P. C. Eklund, D. T. Colbert, R. E. Smalley and R. C. Haddon, *J. Phys. Chem. B*, 2001, **105**, 2525–2528.

33 Y.-P. Sun, W. Huang, Y. Lin, K. Fu, A. Kitaygorodskiy, L. A. Riddle, Y. J. Yu and D. L. Carroll, *Chem. Mater.*, 2001, **13**, 2864–2869.

34 K. Fu, W. Huang, Y. Lin, L. A. Riddle, D. L. Carroll and Y.-P. Sun, *NanoLetters*, 2001, **1**, 439–441.

35 J. E. Riggs, Z. Guo, D. L. Carroll and Y.-P. Sun, *J. Am. Chem. Soc.*, 2000, **122**, 5879–5880.

36 R. Czerw, Z. Guo, P. M. Ajayan, Y.-P. Sun and D. L. Carroll, *NanoLetters*, 2001, **1**, 423.

37 V. A. Basiuk, E. V. Basiuk and J.-M. Saniger-Blesa, *NanoLetters*, 2001, **1**, 657–661.

38 E. T. Mickelson, C. B. Huffman, A. G. Rinzler, R. E. Smalley, R. H. Hauge and J. L. Margrave, *Chem. Phys. Lett.*, 1998, **296**, 188–194.

39 E. T. Mickelson, I. W. Chiang, J. L. Zimmerman, P. J. Boul, J. Lozano, J. Liu, R. E. Smalley, R. H. Hauge and J. L. Margrave, *J. Phys. Chem. B*, 1999, **103**, 4318–4322.

40 H. F. Bettinger, K. N. Kudin and G. E. Scuseria, *J. Am. Chem. Soc.*, 2001, **123**, 12849–12856.

41 P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave and R. E. Smalley, *Chem. Phys. Lett.*, 1999, **310**, 367–372.

42 H. Peng, Z. Gu, J. Yang, J. L. Zimmerman, P. A. Willis, M. J. Bronikowski, R. E. Smalley, R. H. Hauge and J. L. Margrave, *NanoLetters*, 2001, **1**, 625–629.

43 J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley and J. M. Tour, *J. Am. Chem. Soc.*, 2001, **123**, 6536–6542.

44 J. L. Bahr and J. M. Tour, *Chem. Mater.*, 2001, **13**, 3823–3824.

45 P. Allongue, M. Delamar, B. Besbat, O. Fagebaume, R. Hitmi, J. Pinson and J. M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 201–207.

46 V. Georgakilas, K. Kordatos, M. Prato, D. M. Guldi, M. Holzinger and A. Hirsch, *J. Am. Chem. Soc.*.

47 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798–9799.

48 M. Prato and M. Maggini, *Acc. Chem. Res.*, 1998, **31**, 519–526.

49 S. Pekker, J.-P. Salvetat, E. Jakab, J.-M. Bonard and L. Forro, *J. Phys. Chem. B*, 2001, **105**, 7938–7943.

50 Carbon Nanotechnologies Inc., http://www.cnanotech.com.