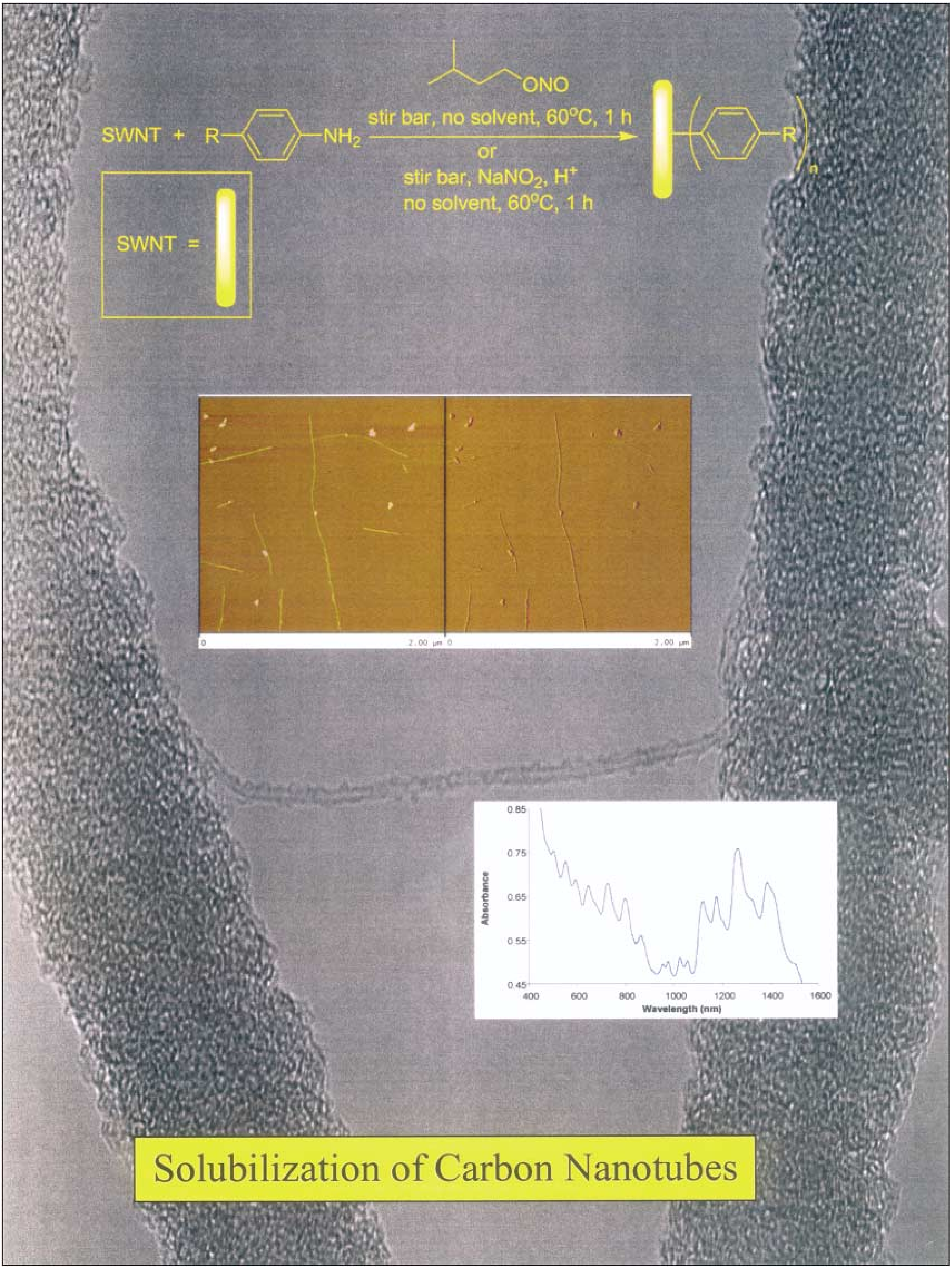

Solubilization of Carbon Nanotubes

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Overcoming the Insolubility of Carbon Nanotubes Through High Degrees of Sidewall Functionalization

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Abstract: The use of carbon nanotubes in materials applications has been slowed due to nanotube insolubility and their incompatibility with polymers. We recently developed two protocols to overcome the insoluble nature of carbon nanotubes by affixing large amounts of addends to the nanotube sidewalls. Both processes involve reactions with aryl diazonium species. First, solvent-free functionalization techniques remove the need for any solvent during the functionalization step. This delivers functionalized carbon nanotubes with increased solubility in organic solvents and processibility in polymeric blends. Additionally, the solvent-free functionalization process can be done on large scales, thereby paving the way for use in bulk applications such as in structural materials development. The second methodology involves the functionalization of carbon nanotubes that are first dispersed as individual tubes in surfactants within aqueous media. The functionalization then ensues to afford heavily functionalized nanotubes that do not re-rope. They remain as individuals in organic solvents giving enormous increases in solubility. This protocol yields the highest degree of functionalization we have obtained thus far—up to one in nine carbon atoms on the nanotube has an organic addend. The proper characterization and solubility determinations on nanotubes are critical; therefore, this topic is discussed in detail.

Keywords: carbon · nanotubes · scanning probe microscopy · single-wall carbon nanotubes (SWNTs) · solubility

Introduction

The highly interdisciplinary field of carbon nanotubes[1,2] has seen progress on many fronts, driven by their extraordinary electrical and mechanical properties.[3,4] For example, nanotubes can be either carbon-based metals or semiconductors,[5,6,7] and these have been used in the construction of nanotube-based transistors[3,8] as well as serving as interconnects in a small integrated circuit.[9] Furthermore, nanotube-based composites show tremendous promise; the lightweight yet strong, flexible,[10] and resilient[11] nanotubes can add fortification to many polymeric structural materials. Slowing the large-scale progression of the field, however, has been the inherent lack of solubility of carbon nanotubes.[12] Single-wall carbon nanotubes (SWNTs), being smooth-sided, highly polarizable compounds, have a reported van der Waals attraction of 0.5 eV per nanometer of tube–tube contact;[13,14] this causes them to exist as ropes (or bundles) in their native state. To generate individually functionalized SWNTs, the thermodynamic drive toward bundling must be overcome. Some strategies employed thus far are polymer wrapping[14] and coating of nanotubes with surfactants.[15–17] Another impediment to materials applications is the poor compatibility between pristine carbon nanotubes and polymer matrices; in many cases, addition of pristine nanotube ropes to polymers causes weakening of the host material.[18–20] Functionalization of SWNTs[21–26] can serve to not only improve their solubility and, therefore, dispersion, but also to create attractive van der Waals interactions between the polymer and nanotube addend.[27] This could be further exploited by tailoring the organic moiety to the host polymer matrix.[18,27] Discussed here are two approaches to the formation of highly functionalized carbon nanotubes: first, a solvent-free process to generate functionalized nanotube ropes that is amenable to large-scale industrial processing and, second, the functionalization of carbon nanotubes dispersed as individuals in aqueous-based surfactants, exemplifying the ultimate in functionalization, whereby there remains little propensity of the nanotubes to re-bundle.

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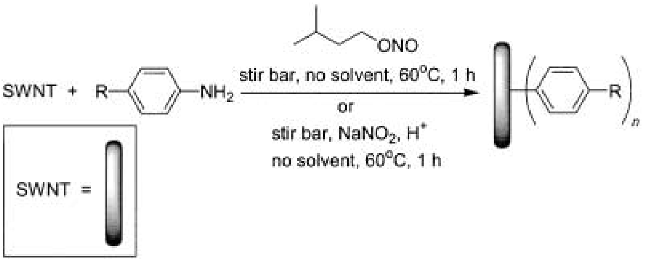
Solvent-Free Functionalization

Prior to our work, the extraordinary amounts of solvent required for dissolution or dispersion of pristine carbon nanotubes limited the efficacy of functionalization reactions; the chemistry was restricted to university laboratories with little hope of becoming useful for industrial-scale processes. Typically, solution-based chemistry employs approximately two liters of solvent per gram of nanotubes coupled with the need for sonication. We recently overcame this restriction by developing a solvent-free[28] functionalization technique,[29] which dispenses with all solvent and sonication needs, and the process is useful for both SWNTs and multiwall carbon nanotubes. Not only does this methodology overcome reaction solubility concerns, but it also offers the added advantages of being scalable, cost-effective, and environmentally benign. The reaction has been conducted on multi-gram scales of carbon nanotubes.

The solvent-free technique employs diazonium chemistry for attaching the organic addends to the sidewalls. In a typical experiment (Scheme 1), purified SWNTs and an appropriate aniline are added to a flask equipped with a magnetic stirring bar. Isoamyl nitrite, which reacts with anilines to give the reactive arenediazonium species, is added to the mixture of solids. As the diazonium salt begins to form and react, a paste results, and the reaction mixture is heated to 60 °C and vigorously stirred. Heating reduces the viscosity of the reaction mixture, and stirring causes de-roping and possibly exfoliation of the larger ropes. Figure 1 shows schematically a plausible mechanism for the reaction. A mechanical force, in this case a stirring bar, applied to a nanotube bundle, distorts the bundle causing bending, buckling, and exfoliation. Exfoliation of the outermost nanotubes from the distorted bundle places the liberated nanotube in the presence of a reactive intermediate. The individual nanotube is then covalently functionalized; this greatly reduces that nanotube's ability to bundle and helps to overcome some of the inherent van der Waals tube–tube attractions. Mechanochemical exfoliation obviates the need for sonication-assisted exfoliation. The solvent-free functionalization methodology gives material as heavily functionalized and soluble as material generated by using standard solution-based reaction protocols. The alkyl nitrite described in Scheme 1 can be substituted with $NaNO_2$ and H^+ (such as sulfuric, acetic, or hydrochloric acid), thereby making the overall process even more industrially attractive. Furthermore, mixing pristine nanotubes/aniline/nitrite for short residence times in a polymer blender, followed by polymer addition, would permit in situ functionalization/blending needed for bulk applications.



Scheme 1. Solvent-free functionalization of carbon nanotubes. R can be various groups including Cl, Br, NO_2, CO_2CH_3, alkyl, OH, alkylhydroxy, oligoethylene glycol, etc.

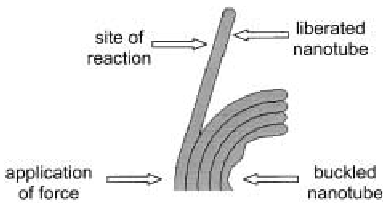


Figure 1. Schematic depiction of the functionalization of carbon nanotubes without solvent.

Although the solvent-free methodology probably gives functionalized bundles, the degree of functionalization obtained gives material with increased solubility (vide infra). In addition, nanotubes with this extent of functionalization disperse in polymers far more efficiently than the pristine SWNTs.[18] Therefore, the solvent-free methodology paves the way for large-scale functionalizations, which would be necessary to generate the quantity of material required to produce fortified structural materials.

Functionalization of Individual (Unbundled) Nanotubes

Another strategy we have employed to overcome the insolubility of carbon nanotubes is the functionalization of individualized SWNTs.[30] In the previous discussion, bundles of nanotubes, treated with reactive reagents, were mechanochemically exfoliated. In that case, as well as in most other functionalization reports, what results are functionalized bundles or mixtures of nanotubes functionalized to various degrees. However, dispersing carbon nanotubes as individuals before a reaction delivers individual functionalized carbon nanotubes. Although not initially applicable to large-scale transformations, it is of fundamental scientific significance for the generation of SWNTs that are incapable of tube–tube re-roping; they clearly overcome the inherent thermodynamic intermolecular cohesive drive (0.5 eV per nanometer)[13,14] to re-bundle.

We have recently demonstrated the individual functionalization reaction by reacting HiPco-produced SWNTs (HiPco = high-pressure carbon monoxide) that were wrapped in sodium dodecylsulfate (SDS). The starting suspensions were generated according to the published procedure[15,30] by sonicating raw material in SDS then centrifuging to sediment the more dense bundles. Decanting the upper 75 % of the supernatant gives suspensions, which predominately consisted of less-dense individualized SWNTs. Functionalization of these stable suspensions of SDS-wrapped SWNTs with diazonium salts gives heavily functionalized material with greatly increased solubility as detailed below. Interestingly, this material disperses as individuals in organic solvent after removal of the surfactant.

Characterization

There are several analytical techniques that must be used in concert to confirm heavy degrees of functionalization. The suite of protocols includes UV and Raman spectroscopy to ensure that the nanotube sidewall is changed through chemisorption (bond formation), and to assess the degree of roping left in the nanotubes. In concert with UV and Raman methods, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS) provide an indication of the degree of functionalization. Transmission electron and atomic force microscopy (TEM and AFM) show sidewall modifications and roping interactions. Without ensuring covalent attachment by UV and Raman spectroscopy, the nanotube could be merely wrapped in polymerized reagent, or more frustratingly, simply mixed with byproducts of the chemical reaction. The use of ^{1}H NMR, XP, and IR spectroscopy alone will not confirm that the organic groups are appended to the sidewalls of the nanotubes, although they can be useful complements to UV and Raman spectroscopy. Note that NMR spectroscopy is usually not very informative, because traces of iron impurities (catalyst for the formation of nanotubes) and the slow tumbling rates of the nanotubes cause severe signal broadening.

After reaction and purification of the functionalized material, the dried solid is characterized. Absorption spectroscopy (Figure 2) confirms covalent sidewall functionalization. Trace A shows the distinct van Hove singularities, which have recently been spectroscopically assigned by nanotube structure,[31,32] of individualized material. Upon covalent functionalization (disruption of the electronic structure), the electrons are localized and all of the transitions disappear (trace B). This complete loss of singularities corresponds to a high degree of covalent modification, which disrupts the extended π-conjugation of nanotubes. Both functionalized bundles and individuals demonstrate a compete loss of singularities, but aggregation or noncovalent functionalization would still have structure albeit not as distinct.

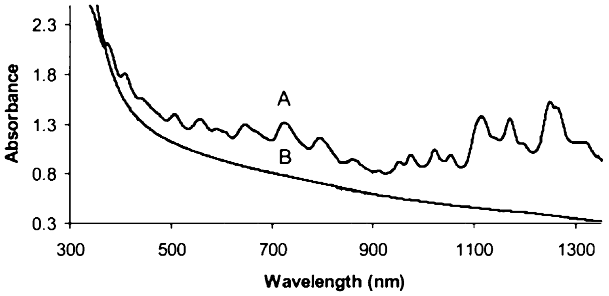


Figure 2. Absorption spectroscopy of A) SDS-coated SWNTs and B) functionalized SWNTs that are SDS-free.

Raman analysis (Figure 3) of functionalized material is another confirmatory tool.[21,26] Highly functionalized carbon nanotubes no longer have the radial breathing modes (250 cm^{-1}) unlike pristine SWNTs. In addition, the disorder mode (1290 cm^{-1}) is much larger for functionalized material than pristine nanotubes. The disorder mode does not increase upon noncovalent functionalization unless processing causes new defect sites on the sidewalls of the nanotubes. Since the resonance Raman enhancement is lost due to functionalization, the intensity of the tangential mode is greatly decreased upon covalent functionalization. Thermally treating (>300 °C) functionalized material regenerates the pristine nanotube structure restoring the radial breathing modes and resonance enhancement of the material, and likewise, greatly decreasing the intensity of the disorder mode. Therefore, the electronic properties can be restored if desired. The Raman spectra shown (Figure 3) correspond to individually functionalized material, which is the most highly functionalized material we have generated thus far.

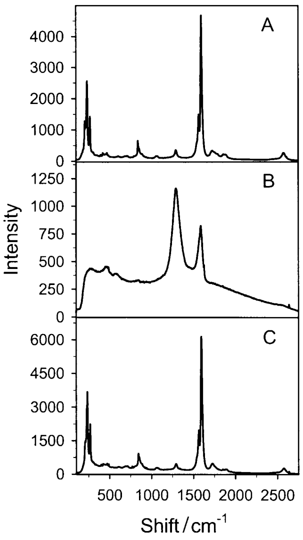


Figure 3. Raman (780 nm excitation) of A) pristine SWNTs, B) functionalized nanotubes, and C) thermally regenerated nanotubes by heat-treating the tubes used in B) to 650 °C.

Once covalent functionalization is confirmed, characterization with TGA (Figure 4) accurately gives the degree of functionalization if the material is free of impurities. This thermal treatment removes the functional organic moieties and the residue that remains is pristine SWNT material.

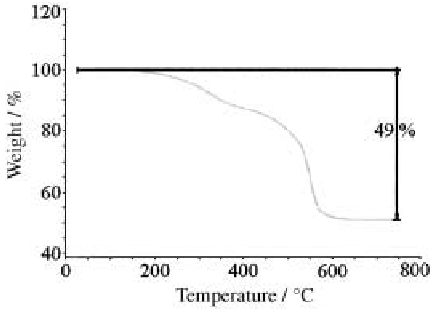


Figure 4. TGA under argon of heavily functionalized 4-chlorophenyl-substitued carbon nanotubes. The addends are removed leaving pristine SWNTs.

Suspending purified, individually functionalized material in organic solvents, casting, drying, and imaging by AFM proves that the SDS-free functionalized nanotubes are either easily exfoliated in organic solvents or incapable of bundling throughout their entire lengths (Figure 5A and B).

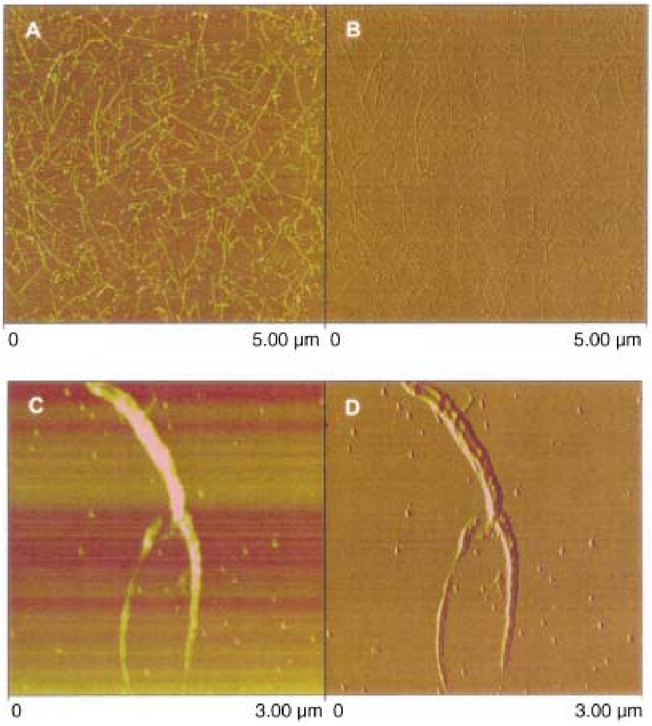


Figure 5. AFM images on mica of the 4-chlorophenyl-substitued nanotubes that were prepared by the SDS/diazonium protocol. Nanotubes were dispersed in DMF, cast, and then evaporated to dryness before imaging. A) Height and B) amplitude of functionalized nanotubes (5 µm per box edge) versus C) height and D) amplitude image of unreacted nanotubes after removal of the surfactant (3 µm per box edge).

Once surfactant is removed from pristine micelle-coated SWNTs, they re-bundle as expected (Figure 5C and D). Interestingly, sidewall addends with increased lengths gives functionalized nanotubes with increased overall diameter, which can be attributed to the increased lengths of the organic moieties appended to the sidewall of the SWNTs.[30] There is a possibility that aryl oligomerization from a nanotube-bound arene can ensue. However, since the addend attachment percentage proceeds to a similar extent even with the 4-*tert*-butylphenyl pendant, polymerization could not be extensive. This is further borne out in the TEM analyses.

Indeed, TEM also confirms the predominance of individual SWNTs resulting from the micelle-based functionalization reaction. Comparing unreacted (Figure 6) and reacted material (Figure 7), the propensity for re-bundling is clear with the surfactant-free pristine tubes; however, analysis of functionalized material reveals the existence of predominately individual nanotubes. Unlike the pristine nanotubes, functionalized material no longer has a smooth-sided sidewall, therefore, bundling is prevented. These have been referred to as "bumps on a log" that inhibit re-roping.

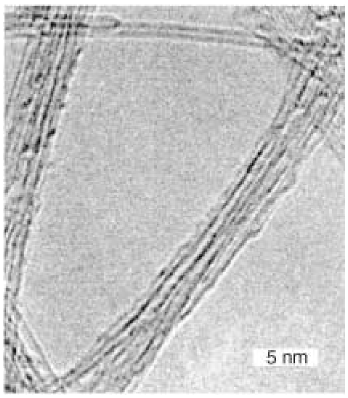


Figure 6. TEM image of unreacted nanotubes after removal of the surfactant. Re-bundling (re-roping) of the nanotubes is clearly observed throughout all imaged locations.

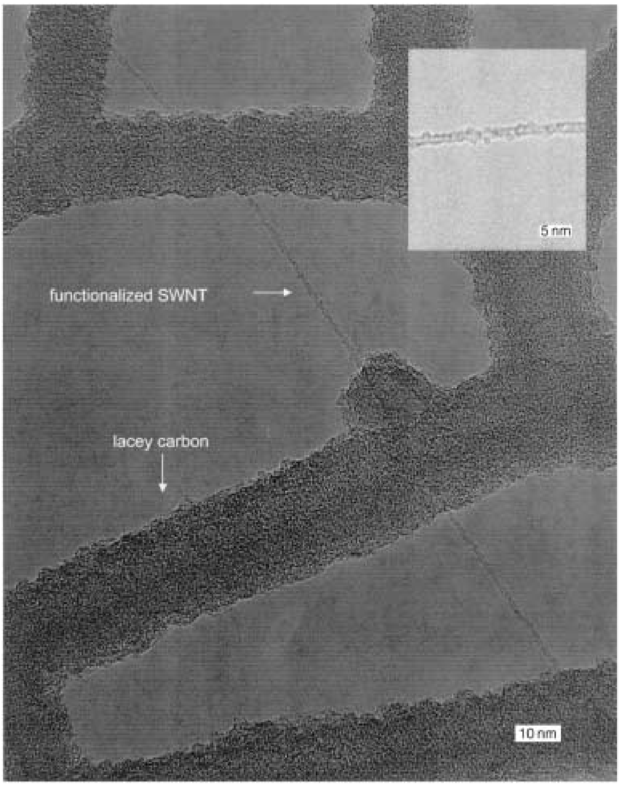


Figure 7. TEM of 4-*tert*-butylphenyl-functionalized carbon nanotubes by the SDS/diazonium protocol. A predominance of individuals is observed throughout the imaged regions. The insert is an expansion wherein the addends are clearly visible and shown to occur at large numbers of locations across the nanotube length. The addends do not appear to be polymeric, but they are individual arenes or short oligomers at most.

Solubility

Solubility numbers that appear in the literature are somewhat ambiguous. There is wide discrepancy between published values; this is due to explainable variations in filtration methods. Without extreme care, this can result in recording of mass inclusive of material that is not nanotube-bound. Once sidewall functionalization is ensured (vide supra), we determine solubility using our published protocols[12] by suspending an excess of the material in an exact amount of the solvent of interest. Typical solvents we use to determine solubility are *o*-dichlorobenzene (ODCB), DMF, chloroform, and THF. Suspensions are obtained by sonicating the material for 30 min, although individually functionalized nanotubes are completely suspended after sonication for 1 min. The material is then gravity filtered through tightly packed fine glass wool. The solution that passes through the glass wool is then further filtered through a 0.2 μm PTFE membrane. The collected solid is removed from the membrane and dried in a vacuum oven at 65 °C overnight. The weight of the dried, filtered material is used to calculate the solubility. Employing this protocol gives solubility values of 0.4 $\mathrm{mg\,mL^{-1}}$ in ODCB in one solvent-free functionalization case compared to 0.095 $\mathrm{mg\,mL^{-1}}$ solubility in ODCB for unfunctionalized SWNTs. This same material had solubility values of 0.03 $\mathrm{mg\,mL^{-1}}$ in THF compared to 0.005 $\mathrm{mg\,mL^{-1}}$ in THF for pristine material. We find that functionalized individual nanotubes (from the SDS protocol) have drastic increases in solubility, whereby one such material had solubility values of 0.7 $\mathrm{mg\,mL^{-1}}$ in ODCB, 0.8 $\mathrm{mg\,mL^{-1}}$ in DMF, and 0.6 $\mathrm{mg\,mL^{-1}}$ in chloroform and THF. Knowing that this material is dispersed as individuals in organic solvent, extreme increases in solubility are observed.[30] Moreover, the solubility in polymers is greatly enhanced for the functionalized materials.[18]

Conclusion

The insolubility and polymer incompatibility of carbon nanotubes has hindered there transitions to bona fide industrial materials applications. Solvent-free functionalization of carbon nanotubes allows for the introduction of organic sidewall addends, which yields material with increased solubility and better dispersion in polymers, and at the same time avoiding the use of the tremendous amounts of solvent typically required. In addition, the solvent-free protocol is capable of functionalizations on a large scale; this should expedite the formation of carbon nanotube-based structural materials. The second protocol described, functionalization of carbon nanotubes dispersed as individuals in surfactants, exemplifies the ultimate in functionalization whereby there remains little propensity to re-bundle. Therefore, the utility of carbon nanotubes may be hastened through high degrees of sidewall functionalizations.

Acknowledgement

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