

Diazonium-Based Functionalization of Carbon Nanotubes. XPS and GC-MS Analysis and Mechanistic Implications

Christopher A. Dyke, Michael P. Stewart, Francisco Maya, and James M. Tour*

Departments of Chemistry and Mechanical Engineering and Materials Science, and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main Street, Houston, Texas 77005, USA

Fax: 713-348-6250

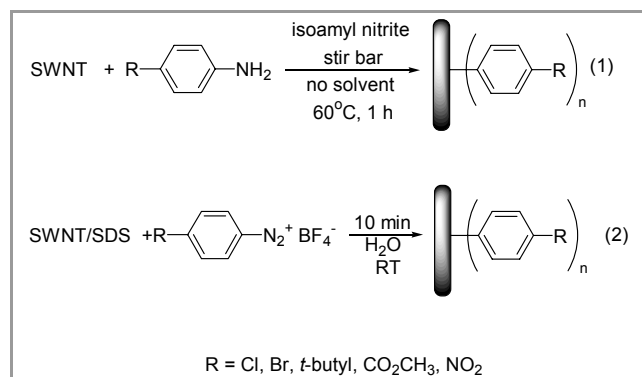
E-mail: tour@rice.edu, www.jmtour.com

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Abstract: A reaction product analysis of single wall nanotubes functionalized by solvent-free and aqueous-based aryl diazonium species is discussed. Both GS-MS on the thermolysis along with XPS analysis of the materials, suggests that the only functionality on the SWNT is the arene group. The mechanism is indicative of an initial aryl radical addition to the nanotube followed by addition of a second aryl radical. A method for defunctionalizing the nanotubes is disclosed wherein the SWNTs are resuspendable in organic solvent.

Key words: nanotube functionalization, fullerene, defunctionalization, aryl radical, carbon nanotubes.

Covalent sidewall functionalization¹ of carbon nanotubes² yields material with increased solubility³ and better dispersibility in polymer matrices.^{4,5} The functionalization process using the diazonium protocol that we developed can be carried out solvent-free using an aniline and an alkyl nitrite or using the pre-formed diazonium salt in organic or aqueous solvent, and the latter works particularly well when the nanotubes are sodium dodecyl sulfate-wrapped (Scheme 1).^{6,7}



Scheme 1 The two reactions studied here for the generation of functionalized single wall nanotubes (SWNTs).

All known nanotube syntheses form mixtures of nanotube types, and though this might not be of concern for structural materials applications, it is a major source of difficulty for electrical or optical uses of nanotubes and SWNTs in particular. Selective sidewall functionalization of one tube type (i.e. metallic nanotubes) to the exclusion of the other types (i.e. semiconducting tubes) could provide a handle for their large-scale separation, and we recently disclosed a method for the selective functionalization of the metallic SWNTs using the aryl diazonium tetrafluoroborates.^{8,9} In the past we have used Raman and UV-Vis-NIR spectroscopies to study the

functionalization products derived from aryl diazonium precursors reacting with SWNTs.^{1,3} Those techniques are well suited for ensuring sidewall derivatization. Here we further investigate the aryl diazonium-based method for attachment of organic moieties to carbon nanotubes with the specific goal of elucidating more mechanistic details for the functionalization process by using x-ray photoelectron spectroscopy (XPS) on the functionalized SWNTs and mass spectrometric analysis of the functionalized nanotube thermolysis products. We also disclose a protocol for the removal of the sidewall addends while maintaining their suspendibility in organic solvents.

Regeneration of the pristine-like nanotube structure becomes of paramount importance if covalent functionalization is used as a handle for separation or for controlled manipulation of material, particularly when the original extended π -electron-derived optical or electronic properties are required for the ultimate desired function. We have shown that functionalized material treated thermally, in the dry state, in an inert atmosphere, defunctionalizes to regenerating the pristine-like SWNT structure.^{6,7,10} However, material treated thermally in the dry state is intractable; it can not be resuspended in organic solvent even with extended sonication. Two mechanisms exist for explaining the loss of solubility. First, covalently crosslinking of multiple nanotubes might ensue during thermolysis via radical reactions. Or when the material is annealed, the defects are moved to the ends of the nanotube leading to low defect sidewalls, giving bundled material energetically difficult to unbundle. Nanotubes have a reported van der Waals attraction of 0.5 eV per nanometer of tube-tube contact.¹¹

The above-identified problem with dispersing thermally treated SWNTs is exemplified in the following study (all reactions here were conducted with purified HiPco SWNTs).¹ Thermogravimetric analysis (TGA) of heavily functionalized (4-chlorophenylene) nanotubes⁷ showed 49% weight loss (Figure 1), which corresponds to 1 in 9 carbons on the nanotube bearing an aryl moiety appended. Comparing the Raman spectrum of the pristine (unreacted) SWNTs (Figure 2A) with that of the 4-chlorophenylene-functionalized material (Figure 2B), the characteristic spectroscopic details for covalent functionalization can be seen.^{1,3} (Note that we are using here a 633 nm excitation which probes the metallic and semiconducting tubes, whereas 780 nm excitation, which we

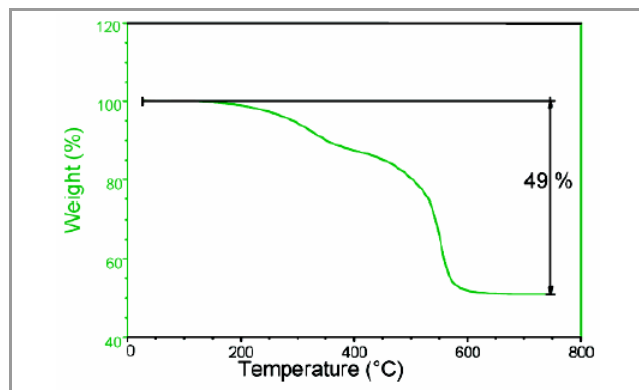


Figure 1 TGA (10°C/min to 650°C, Ar) of heavily functionalized SWNTs containing 4-chlorophenylene addends by treatment of micelle-coated SWNTs with 4-chlorophenyl diazonium tetrafluoroborate. The material had been washed free of surfactant prior to thermalization.⁷

often used in the past, would probe only the semiconducting tubes in this region.) Upon neat thermal treatment in Ar at either 650°C or 450°C for extended periods, the addends could be removed and the Raman spectra, Figures 2C and 2D, respectively, resembled that of the pristine SWNTs shown in Figure 2A. However, attempts to disperse the defunctionalized SWNTs in DMF were unsuccessful, even with extended sonication. Using this same heavily functionalized material (X mg), but dissolving it *ortho*-dichlorobenzene (ODCB, Y mL) prior to thermal treatment and heating the solution to 450°C for 3 h in a screw-cap tube gave defunctionalized material as seen in Figure 2E. Raman of this material confirmed significant defunctionalization, albeit not completely pristine-like. However, unlike thermal treatment in the dry state, this protocol gives material with similar solubility to the starting pristine SWNTs.

Thermal treatment of material dispersed in ODCB solvent possibly prevents nanotube radicals from combining to form nanotube dimers; instead, two radicals on the same nanotube might combine by extended conjugation to regenerate the C–C double-bond. We analyzed the byproducts of the ODCB-thermalized reaction of 4-*tert*-butylphenylene-functionalized SWNTs by GS-MS of the ODCB solution (Scheme 2).⁷ Two biphenyls, **1** and **2**, were generated by the addends coupling with the solvent which substantiates (a) the *tert*-butylphenylene attachment to the nanotube and (b) the reactive nature of the moiety as it is evolved from the nanotube. Interestingly, there was no discernible di(*tert*-butyl)biphenyl present in the reaction mixture, so the addends did not evolve in pairs. If the addends had evolved as aryl anions, reaction with solvent would likely have led to chloride substitution on the ODCB. Expulsion as the cation would have led to a highly reactive species that could afford the product observed in Scheme 2. However, thermolytic cleavage most likely proceeds via a homolytic process.

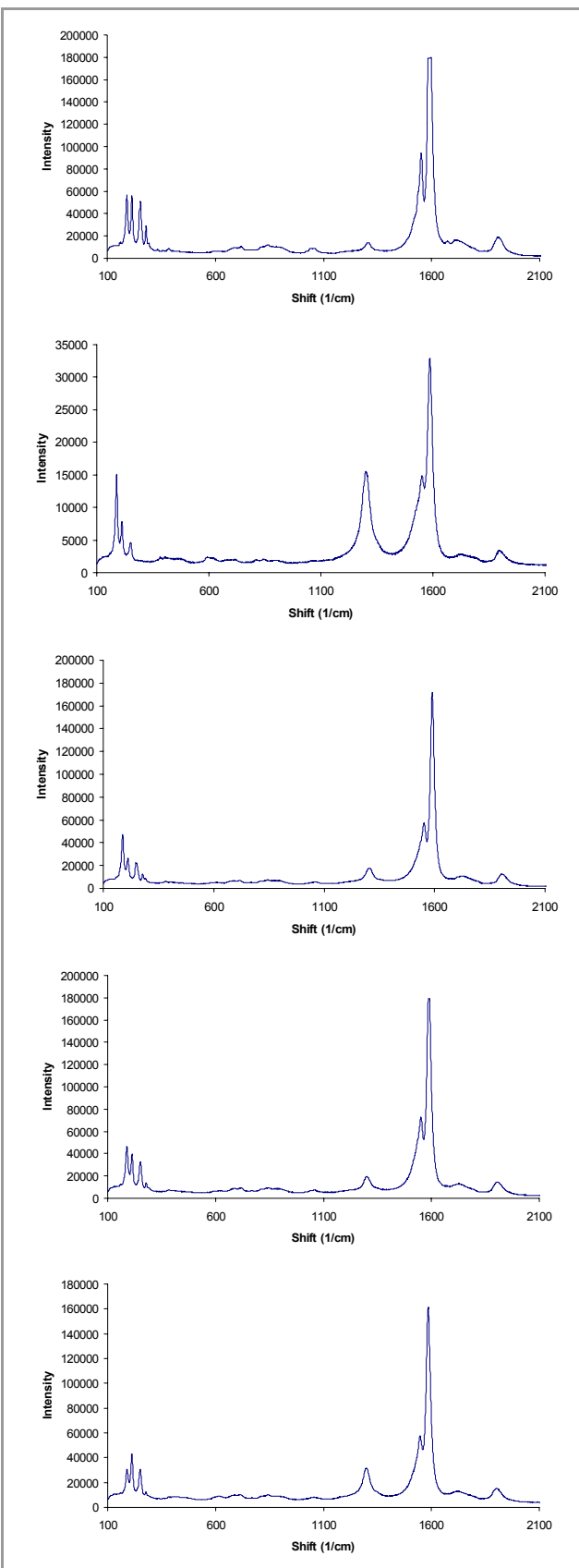
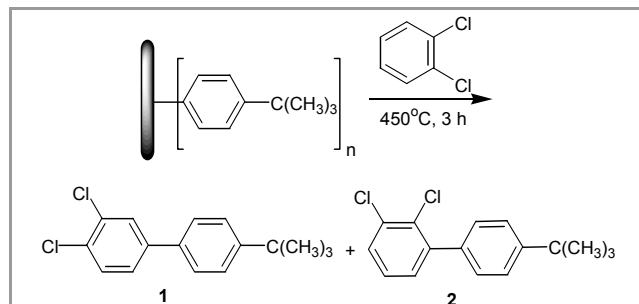


Figure 2. Raman analysis (633 nm excitation). (A) Pristine (unreacted) SWNTs. (B) Heavily functionalized SWNTs containing 4-chlorophenylene addends by treatment of micelle-coated SWNTs with

4-chlorophenyl diazonium tetrafluoroborate. This corresponds to the material used for the TGA in Figure 1. (C) The same material as in Figure 2b but after neat thermal treatment at 10°C/min to 650°C in Ar, (D) The same material as in Figure 2b but after neat thermal treatment at 10°C/min to 450°C and holding at 450°C for 2 h. (E) The same material as in Figure 2b but after thermal treatment in ODCB at 450°C for 3 h.



Scheme 2. Thermolysis of 4-*tert*-butylphenylene-functionalized SWNTs (prepared by the SDS-coated SWNT/H₂O protocol)⁷ in ODCB (solvent) afforded defunctionalized SWNTs and two discernable volatile products, the biphenyls shown, by GC-MS analysis of the reaction mixture.

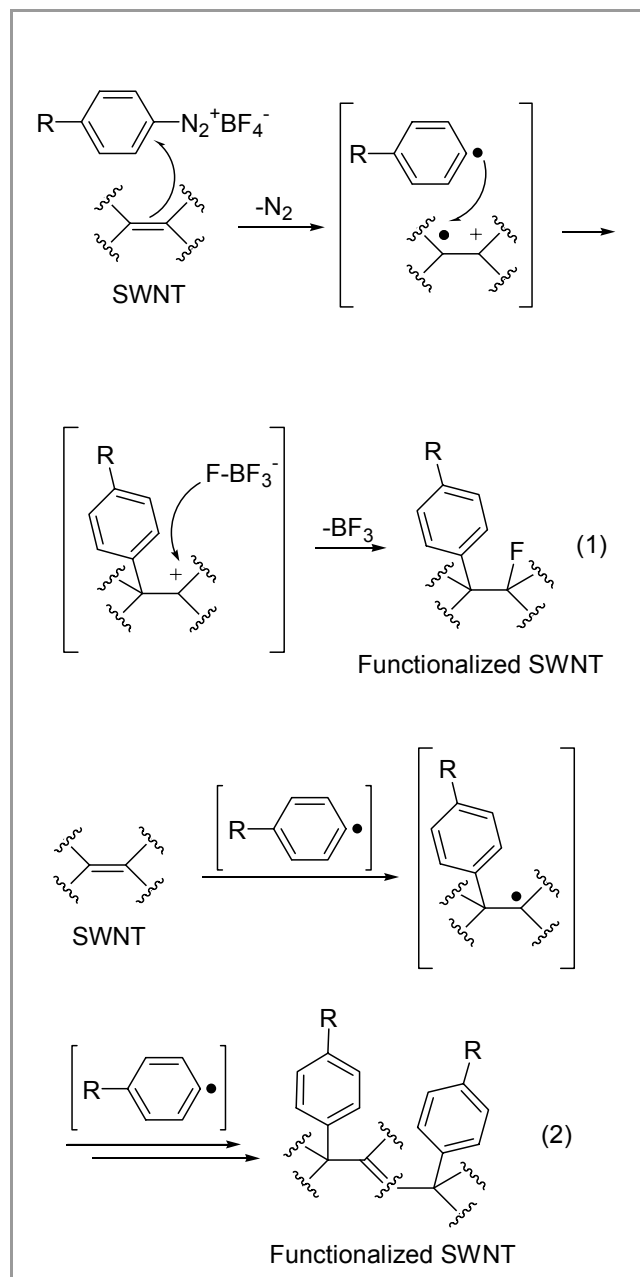
In a further effort to rationalize the reaction process between the diazonium species and the SWNTs, we considered the mechanisms shown in Scheme 3. Eq 1 shows that the functionalization of a SWNT diazonium species might arise by electron addition from the SWNT to the arene to form the SWNT-radical cation and a nearby aryl radical with evolution of dinitrogen. Radical-radical coupling would afford the arene-SWNT-cation, which could react with any nucleophile in solution, most probably fluoride (adjacent or extended by delocalization) in this case. One would expect the same product (addition of arene and fluoride) as that shown in eq 1 of Scheme 3 if the SWNT were to react with the aryl cation. Eq 2 of Scheme 3 shows the possible reaction of the SWNT with the aryl radical (generated spontaneously from the diazonium species) to form an arene-SWNT-radical that could vicinally couple with another aryl radical, or after delocalization as shown.

In order to check for the presence of fluoride or nitrogen species resulting from the diazonium reaction, functionalized nanotube samples were analyzed by XPS. Samples were functionalized with *p*-*tert*-butylphenylene groups using two different methods: *in situ* generation of a diazonium salt in a solvent-free reaction with nanotubes (isoamyl nitrite and 4-*tert*-butylaniline, Scheme 1, eq 1)⁶ (XPS spectra in Figure 4A) and via addition of a stable diazonium tetrafluoroborate to SDS-treated nanotubes in solution at pH 10^{7,8} as in Scheme 1 eq 2 (XPS spectra in Figure 4B) and comparison to the XPS spectra of the pristine SWNTs (Figure 4C). In Figures 4A-C, the F 1s regions are compared. In both reacted samples, only trace amounts of inorganic fluorine are present. XPS studies of fluorine atoms covalently bound to the sidewall of a carbon nanotube typically show a strong signal at a binding energy of 690 eV or higher, depending on the degree of chemical bonding.¹³ Although the

isoamyl nitrite reaction has no added fluoride while the BF₄⁻ process has significant of F⁻ present for reaction with the nanotubes, there appears to be little difference in the fluoride content between the two samples which suggest that a nanotube cation (Scheme 3 eq 1) is not generated during the functionalization or that the cation is simply not a recipient of F⁻ due to its delocalization. In fact, the fluoride-free reaction appears to have trace amounts more of fluoride, but both levels are barely detectable (< 1 wt %) above the noise range, as in the pristine sample. The fluoride traces might arise from impurities when filtered through PTFE (Teflon®).^{6,7,8} Likewise, an aryl cation formation is unlikely. However, this analysis would be consistent with the aryl radical reacting directly with the SWNT, as in Scheme 3 eq 2. The GC-MS studies did not show the arene addends evolving as dimeric species; therefore, delocalization prior to the second aryl radical addition may be the sterically favored route as suggested in Scheme 3 eq 2. Furthermore, the C 1s and N 1s are as expected, the latter suggesting that indeed dinitrogen was lost prior to arene addition to the SWNTs.

The structure of the diazonium entity in water is largely dependent on the pH of the solution. We therefore further investigated the pH dependent reaction of the SWNT functionalization process in aqueous micellar solution.^{7,8} These reactions are typically conducted at pH 10 (Gomberg-Bachmann conditions)¹⁴ and they are complete within 10 min. At pH 7, the reaction is equally fast, but at pH 2, functionalization does not occur. Analysis of the diazonium salt by ¹H NMR in D₂O was conducted to determine the structure of the functionalizing diazo entity. NMR of the diazonium salt is unaffected in D₂O upon acidification with HCl, however, addition of DO⁻ to the salt in D₂O shifts the aryl protons *ortho* to the diazonium group upfield by 1.6 ppm (from 8.4 ppm to 6.8 ppm). Attempts to characterize this entity led to decomposition, but the NMR probably corresponds to diazotate formation (Scheme 4 eq 1). Extraction of this solution with organic solvents gives a highly colored, neutral entity, which decomposes rapidly. Performing the same experiment, adding hydroxide to the dissolved diazonium salt in organic solvents where radical traps such as THF and acetonitrile (as opposed to water) give the hydro-dediazotiation product with instant gas evolution. The mechanism of the Gomberg-Bachmann reaction has been investigated by Rüchardt and Merz, and they invoke the neutral, reactive diazoanhydride.¹⁵ Formation of this entity appears to be consistent with our findings. For the functionalization of carbon nanotubes dispersed as individuals in aqueous sodium SDS solution, the neutral diazoanhydride, once formed, could migrate into the micelle and comes in close proximity to the sidewall of the nanotube. The anhydride then decomposes to the aryl radical, which reacts with the carbon nanotube giving an aryl-SWNT-radical (Scheme 2 eq 2) that can then react with another aryl radical. The oxygen radical can abstract a hydrogen atom from the micelle, further react with the diazonium salt under the basic conditions, and thereby giving the

diazotate and ultimately generating another equivalent of the diazoanhydride (Scheme 4 eq 1).



Scheme 3. Eq 1 shows that functionalization of SWNTs by diazonium species could arise by electron addition from the SWNT to the arene. Eq 2 shows the possible reaction of the SWNT with the aryl radical.

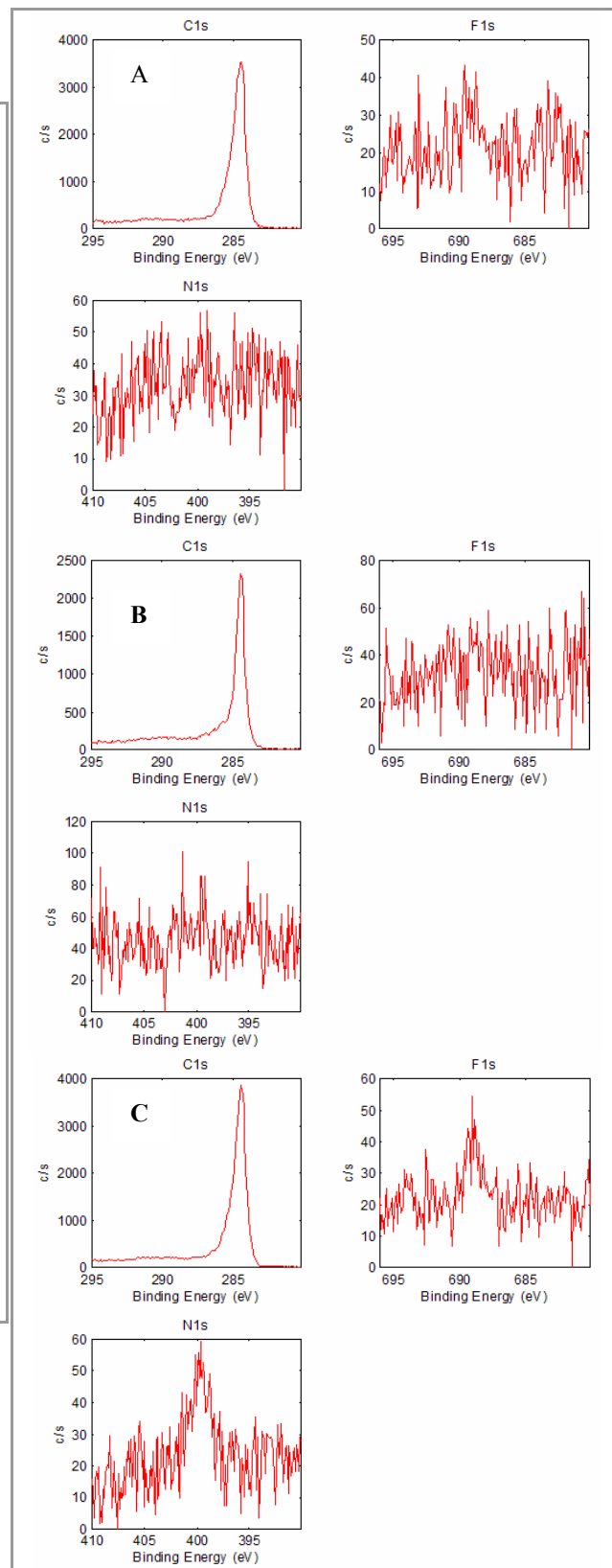
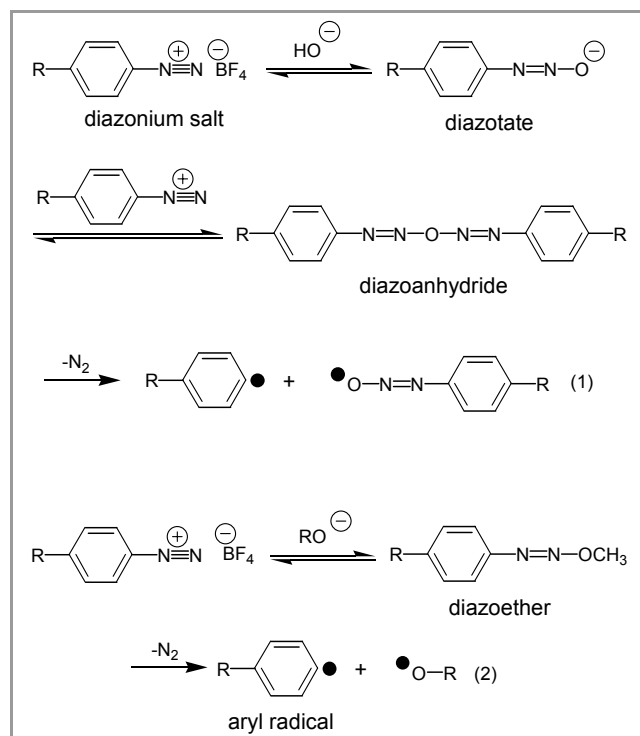


Figure 4. XPS analysis of A) solvent-free functionalized carbon nanotubes using isoamyl nitrite and 4-*tert*-butylaniline, and B) nanotubes functionalized as individuals in aqueous solution using SDS-treated nanotubes in solution at pH 10 with 4-*tert*-butylphenyldiazotetrafluoroborate and C) pristine SWNTs.

Treating an aniline with isoamyl nitrite also functionalizes carbon nanotubes by generating the reactive diazo entity in situ. The aniline attacks the nitrite giving the diazonium, water and alkoxide. The alkoxide either reacts with the diazonium giving a diazoether or deprotonates water giving hydroxide, which reacts with the diazonium leading to diazoanhydride formation (Scheme 4 eq 2). Both intermediates lead to aryl radical formation (Scheme 4). Hence the classical mechanism of the Gomberg-Bachmann seems consistent in the functionalizations here.^{14,15} Based on our SWNT-chemoselective studies,⁸ this would also imply that the metallic SWNTs are far more prone to reaction with aryl radicals than are semiconducting tubes.



Scheme 4. Typical aryl diazonium salt decomposition pathways.^{14,15}

In summary, a combination of GS-MS on the thermolysis products of aryl diazonium-based functionalized SWNTs, along with XPS analysis of the materials, suggests that the only functionality on the SWNT is the arene group. The mechanism is indicative of an initial aryl radical addition to the nanotube followed by addition of a second aryl radical.

Acknowledgment

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