Nanotube Functionalization

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An Atom-Economical Approach to Functionalized Single-Walled Carbon Nanotubes: Reaction with Disulfides[**]

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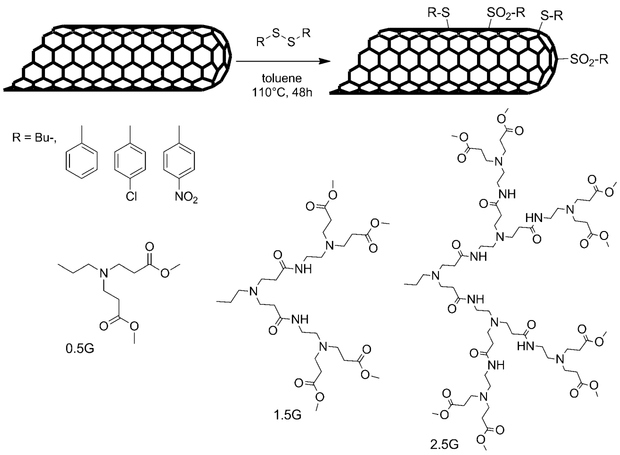
Owing to their unique structure, thermal stability, and mechanical and electronic properties, single-walled carbon nanotubes (SWCNTs) have been a subject of continuous and intense interest.[1] However, various applications in many fields, such as molecular electronics, solar cells, and nanomedicine, often require the development of reproducible protocols for the chemical modification of SWCNTs.[2] In fact, one of the main drawbacks of the use of SWCNTs is their tendency to aggregate and intrinsic poor solubility, which prevent their manipulation and limit their potential. To date, several methods have been described for the chemical functionalization of SWCNTs;[2] however, new versatile and reliable methods are still needed. We focused our attention on disulfides, which are a very useful family of compounds owing to the presence of the flexible S–S bond. Disulfides can be prepared readily from the corresponding thiols;[3] thus, a wide range of substrates are accessible. In this study, we used very mild and reproducible conditions for the production of a wide variety of functionalized SWCNTs (f-SWCNT).

Pristine HiPco SWCNTs (p-SWCNTs, prepared with high-pressure carbon monoxide, HiPco) were treated with disulfides in deoxygenated toluene at reflux (Scheme 1). The reaction with diphenyl disulfide was monitored for 48 h by means of thermogravimetric analysis (TGA) and Raman spectroscopy, which showed changes in weight loss and in the relative D- and G-band intensities, respectively (Figure 1).



Scheme 1. Chemical functionalization of SWCNTs through the addition of disulfides.

TGA showed an increase in weight loss in the range 250–700 °C from 1.7 % after 6 h to 18.8 % after 48 h (see Figure S1 in the Supporting Information) and thus clearly indicated the detachment of organic fragments covalently linked to the

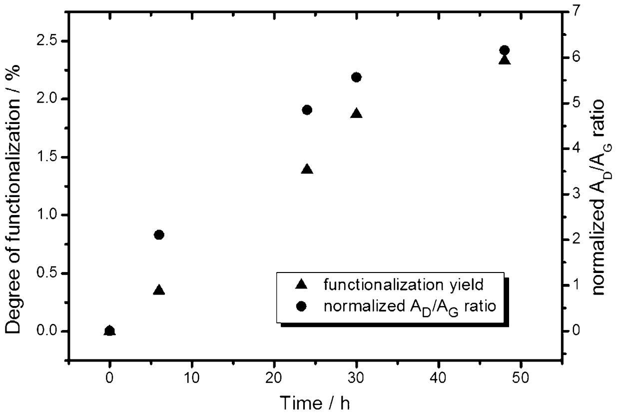


Figure 1. Comparison of the degree of functionalization (determined by TGA) with the normalized A_D/A_G ratio (from Raman spectra) for the reaction of SWCNTs with $(PhS)_2$ as a function of the reaction time.

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nanotube surface.[4] The amount of weight loss at 700 °C, at which temperature all the organic material has thermally decomposed, whereas the SWCNTs are still intact, can be used to calculate the degree of functionalization. In practice, we assumed that the attachment of an organic group to each carbon atom in the SWCNT structure would correspond to a degree of functionalization of 100 %. We thus described the degree of functionalization of our products with reference to a fully functionalized SWCNT: a degree of functionalization of 1 % means covalent attachment of one organic group per 100 carbon atoms of the SWCNT skeleton (see the Supporting Information for details).

We also tested several aliphatic and aromatic disulfides, including cystamine-core polyamidoamine (PAMAM) dendrimers[5] from generation 0.5 to 2.5 (Scheme 1 and Table 1). Both aliphatic and aromatic disulfides reacted well (see Figure S2 for the corresponding TGA). Interestingly, cystamine dendrimers afforded highly functionalized dendron-decorated SWCNTs (Table 1, entries 5–7). SWCNTs modified with these dendrimers up to the 2.5 generation could be synthesized and have potential for further applications.[6] TGA of the dendrimer-modified nanotubes showed increasing weight loss in good accordance with the increasing molecular weight of nanotubes modified with higher dendrimer generations (Figure 2 a): remarkable values of 53.7 and 72.3 % were found for the 1.5 and 2.5 generations, respectively. These weight losses were estimated in the range 200–700 °C, since PAMAM dendrimers start decomposing above 150 °C.[7]

Table 1: Screening of different disulfides in the reaction with pristine HiPco SWCNTs (p-SWCNTs).

Entry	Substrate[a]	Weight loss %[b]	A_D/A_G[c]	f [%][d]	S/C [%][e]	S_{red}/S_{ox}[e]
1	$(nBuS)_2$	6.8	3.14	0.83	0.4	0:100
2	$(PhS)_2$	18.8	6.16	1.97	1.35	0:100
3	$(4\text{-}ClC_6H_4S)_2$	13.2	6.57	1.04	1.97	0:100
4	$(3\text{-}NO_2C_6H_4S)_2$	21.3	5.50	1.74	3.98	0:100
5	PAMAM 0.5G[f]	16.3	3.40	1.05	1.30	87:13
6	PAMAM 1.5G[f]	53.7	3.26	2.10	1.97	45:55
7	PAMAM 2.5G[f,g]	72.3	3.92	2.10	1.49	47:53

[a] Reaction conditions: p-SWCNTs (10 mg, 0.83 mmol), disulfide (2.2 equiv), deoxygenated toluene (100 mL), 110 °C, 48 h. [b] Weight loss was measured by TGA in the temperature range between 250 and 700 °C; 6.4 % was subtracted from the measured weight loss (loss of p-SWCNT). [c] Values are the ratios $A_{D(sample)}/A_{G(sample)}$ normalized with respect to the ratio A_{D0}/A_{G0} of the p-SWCNTs. [d] Degree of functionalization (see the Supporting Information for its calculation). [e] The values were obtained by XPS analysis; S_{red} and S_{ox} indicate the amount of sulfide and sulfone in the sample. [f] Weight loss was measured by TGA in the temperature range between 200 and 700 °C. [g] The reaction was carried out with 1.65 equivalents of the disulfide (1.36 mmol).

Raman spectroscopy is an established useful tool for the structural investigation of sidewall-functionalized SWCNTs.[8] The covalent attachment of functional appendages leads to the rehybridization of sidewall carbon atoms, as reflected by an increase in the intensity of the D band (at approximately 1300 cm^{-1}) with respect to that of the graphitic band (G band, at approximately 1590 cm^{-1}). The ratio of the intensity of the D and G bands (A_D/A_G) can be taken as another measure of the degree of functionalization. The A_D/A_G ratios were compared to the A_{D0}/A_{G0} values of the starting SWCNTs. In the case of diphenyl disulfide, the normalized A_D/A_G ratio increased strongly within 24 h of reaction to reach a significant value after 48 h (see Figure S3). PAMAM-functionalized SWCNTs also showed good normalized A_D/A_G ratios (in the range 3.40–3.92) in the Raman spectra for all dendrimer generations (Figure 2 b). Nevertheless, the SWCNTs proved to be more susceptible to functionalization with aromatic disulfides than with the aliphatic disulfides: with aromatic disulfides, higher normalized A_D/A_G ratios, in the range 5.50–6.57, were observed (see Figure S4).

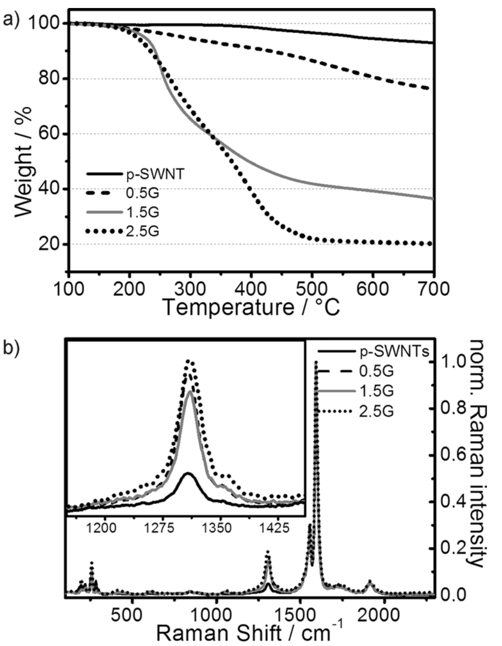

Figure 2. a) TGA and b) Raman spectra recorded at 633 nm of p-SWCNTs and f-SWCNTs functionalized with cystamine-based dendrimers. The inset shows a magnification of the D band.

The influence of the amount of disulfide on the degree of functionalization was also tested with diphenyl disulfide: the best result after 24 h was obtained with 2.2 equivalents of the reactant. Worse results were obtained with 1.1, 4.4, and 11 equivalents of $(PhS)_2$ (see Figure S5). The functionalization reaction can be reversed to provide nonfunctionalized SWCNTs (or defunctionalized SWCNTs, df-SWCNTs) by heating the f-SWCNTs at 400 °C for 4 h. For example, thermal treatment of the f-SWCNTs that were functionalized by treatment with $(PhS)_2$ led to a substantial decrease in the intensity of the D band and a decrease in the normalized A_D/A_G ratio from 6.16 to 1.20, which is close to the value of the initial pristine tubes (see Figure S6). This behavior is common to most functionalized SWCNTs.[9]

A plausible mechanism for the title reaction would be the homolytic cleavage of the weak sulfur–sulfur bond. The resulting thiyl radical would then attack the extended π system of the SWCNTs. However, it has been reported that the thermal homolysis of disulfides at 100 °C in solution takes place with very low rate constants.[10] To shed light on this issue, we carried out two parallel reactions by mixing two different disulfides (dibutyl and bis(3-nitrophenyl) disulfide) in the absence and in the presence of p-SWCNTs in toluene at reflux for 48 h. In both cases, the unsymmetrical disulfide was isolated. However, this disulfide was obtained in just 2.8% yield in the absence of SWCNTs, and in an improved yield of 16% in the presence of SWCNTs (see Figure S7 for details). Hence, the p-SWCNTs seem to promote homolysis of the disulfides to afford a higher concentration of thiyl radicals. To investigate our hypothesis of a radical route, we carried out a reaction in the presence of a radical trap. When SWCNTs were treated with diphenyl disulfide under the optimized conditions in the presence of 2,6-di-*tert*-butylphenol, almost no nanotube functionalization occurred. Thus, thiyl radicals may be involved in the process (see Figure S8).

An important feature of the reported reaction is that the process proved to be atom-economical. When the reaction is finished, the unreacted disulfide can be recovered unmodified by simple filtration and potentially reused for other reactions. Recovery of the disulfide was shown for diphenyl disulfide and cystamine PAMAM 0.5G (see Figures S9 and S10) and is of particular interest when expensive disulfides or those whose synthesis is time-consuming are used.

The f-SWCNTs showed improved solubility in organic solvents, such as *N*-methyl-2-pyrrolidone (NMP).[11] The corresponding absorption spectra of some derivatives are displayed in Figure S11 a,b, along with the spectra of the dendrimer-modified nanotubes dispersed in MeOH.

X-ray photoelectron spectroscopy (XPS) provided information about the superficial chemical composition and bonding of the cystamine-dendrimer-functionalized nanotubes. XPS is a useful technique for surface rather than bulk analysis but may give a consistent picture when used for a homogeneous series of samples. In Table 1, the S/C ratio is reported for different f-SWCNTs (see Table S1 for the binding energies and relative populations of the different atoms as well as the atomic ratios). Figure 3 a displays the survey spectra of the PAMAM-containing SWCNTs (generations 0.5, 1.5, and 2.5) along with that of the pristine nanotubes. The pristine nanotubes show a high content of metal nanoparticles (catalyst), as indicated by the steep increase in the background above 700 eV as a result of the emission of Fe 2p and probably Co 2p photoelectrons. However, as the generation of the attached dendrimer grows, the metal content seems to decrease considerably.

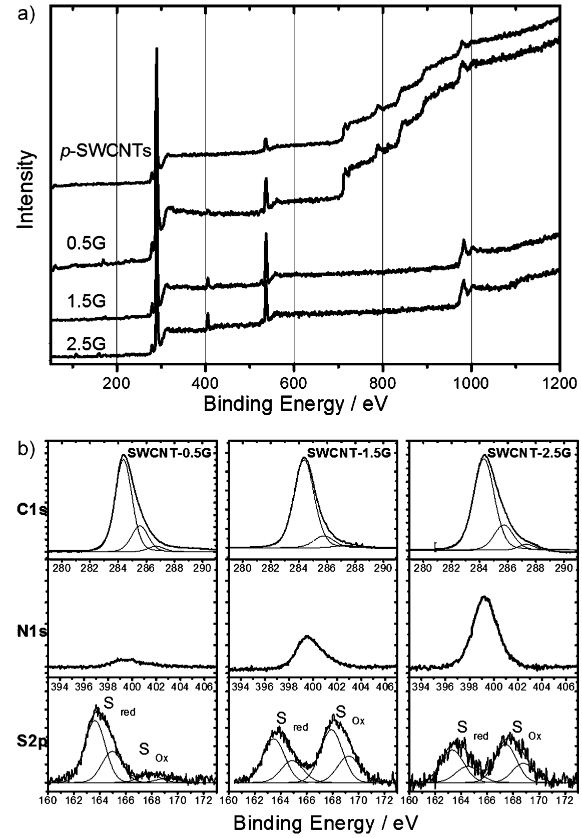

Figure 3. XPS spectra of pristine and dendrimer-funtionalized nanotubes. a) Survey spectra (the traces have been shifted for clarity). b) C 1s, N 1s, and S 2p high-resolution spectra.

In the C 1s region of typical high-resolution spectra of f-SWCNTs (Figure 3 b), the peaks were fitted with three components. The main contribution appears at 284.4 and is generally assigned to the C(sp^2)–C(sp^2) bonds of graphitic carbon in the SWCNT structure. The minor peaks at 285.7 and 286.9 are attributed to C(sp^3)–C(sp^3) groups and to oxygen-containing C(sp^2) and C(sp^3) atoms, respectively.[12] In the normalized N 1s region at 399 eV (Figure 3 b), the peak intensity increases across the dendrimer series from 0.5G to 2.5G, in agreement with the higher content of nitrogen atoms in the higher-generation dendrimers. Although the N/S and S/O ratios do not correspond to the exact stoichiometry of the functionalized nanotubes, especially for the higher-generation dendrimers, their increase across the generations is clear. Indeed, when the attached molecules become big, the random spatial arrangement makes the XPS ratios useless for "absolute" quantification but good for comparison purposes. Finally, high-resolution S 2p core-level spectra for the same functionalized samples (Figure 3 b) provide insight into the process underlying the title reaction. Each sulfur peak was fitted with one doublet owing to the presence of S2p$_{3/2}$ and S2p$_{1/2}$ components originating from the spin–orbit splitting effect. A splitting of 1.2 eV and a 2:1 (S 2p$_{3/2}$/S 2p$_{1/2}$) peak-area ratio were taken for the fitting. Interestingly, two doublets were found in the S 2p region, the respective intensities of which changed along the series. The first doublet, with the S 2p$_{3/2}$ peak centered at around 164 eV, is attributable to sulfur in its sulfide form directly bonded to the graphitic backbone,[13] whereas the S 2p$_{3/2}$ peak centered at around 168 eV corresponds to sulfur in its sulfone form, $-SO_2-$.[14] Hence, during the functionalization process, some of the sulfur atoms linked to the nanotube surface are oxidized to their sulfone form, probably as a result of the action of oxygen present in the interstitial sites of the SWCNT bundles (Table 1). On the other hand, in the XPS spectra of SWCNTs functionalized with the aromatic substrates diphenyl, bis(4-chlorophenyl), and bis(3-nitrophenyl) disulfide, all sulfur is in the sulfone form (see Figure S12 for an example). Interestingly, in the latter two substrates, the atomic ratio between sulfur and the second heteroatom was very close to the ideal value of 1 (N/S, 1.10; Cl/S, 1.12; see Table S1).

To confirm the reliability of the XPS data, we determined the sulfur concentration of selected samples quantitatively by means of bulk elementary analysis (see Table S2). Both the S/C ratios and the degree of functionalization obtained by the two different methods were in good agreement, with differences within 10%. This finding confirms the results recently reported for the radical addition of xanthates to multiwalled carbon nanotubes and SWCNTs.[15]

In conclusion, we have presented a detailed study on a novel, straightforward, fast, and reliable protocol for nanotube functionalization. This new process shows the further advantage of atom economy, since it allows the recovery and reuse of unreacted disulfides. As well as simple aliphatic and aromatic disulfides, we successfully tested cystamine dendrimers of different generations as substrates and obtained highly loaded SWCNTs. TGA and Raman analysis showed the high degree of functionalization achieved. Finally, XPS revealed that partial or total oxidation of the anchoring sulfur atoms to sulfone groups takes place during the reaction. The reported method paves the way toward the preparation and practical application of novel, readily processable nanotube-based materials.

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