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Cycloaddition of benzyne to SWCNT: towards CNT-based paddle wheels

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The cycloaddition of benzyne to SWCNT has been carried out for the first time. Raman spectroscopy, TGA, HR-TEM, UV-vis-NIR as well as XPS have been used for products characterization.

Carbon Nanotubes (CNTs) have emerged as central building blocks in nanoscience as a result of their unique mechanical, geometric, thermal, and electrical properties opening doors to their use in electronic, optical, magnetic and mechanical applications. Chemical functionalization¹ of CNTs allows both to increase their solubility and to modulate their properties and although some work has been done along the last years on the chemistry of CNTs, the establishment of new protocols for their functionalization is still needed. Functionalized CNTs, due to their modulated properties, potentially offer possibilities for unprecedented applications providing opportunities for the fabrication of novel nanodevices; in this respect, it has been theoretically suggested that it may be possible to make paddle wheels by bonding rigid molecules (gear teeth) such as benzene onto CNTs (Fig. 1).²

Following our research on SWCNT functionalization^{3,4} and aryne cycloadditions^{5,6} we report herein the functionalization of SWCNT by cycloaddition of benzynes. To this aim arynes



Fig. 1 Proposed molecular paddle wheels² (reprinted with permission from IOP Nanotechnology) (left). Cycloaddition product of benzyne to SWCNT (right).

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were generated by two different procedures (Scheme 1): (i) thermal decomposition of benzenediazonium 2-carboxylate $(2)^7$ and (ii) fluoride induced elimination of TMS and triflate from 2-(trimethylsilyl)aryltriflates 3.8 By procedure (i), after heating at 80 °C a suspension of benzenediazonium 2-carboxylate (2) and SWCNT in o-dichlorobenzene (ODCB) for 4 h followed by filtration and centrifugation (see Experimental in ESI^t) covalent functionalization of SWCNT was achieved and proved by Raman spectroscopy and TGA as indicated below (see ESI[‡], Fig. S1 and S2, respectively). Following procedure (ii) a solution of 2-(trimethylsilyl)aryl trifluoromethanesulfonate 3 in acetonitrile (CH₃CN) was added to a suspension of SWCNT in ODCB under Ar; then 18-crown-6 ether and dry CsF were added and the mixture was refluxed overnight affording f-SWCNT 1. It should be indicated that previous studies by Dyke and Tour using 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and TBAF under solvent-free conditions afforded unfunctionalized SWCNT only.9 f-SWCNT 1a and 1b were characterized by Raman spectroscopy, TGA, HR-TEM, UV-vis-NIR, FTIR as well as XPS techniques.

Fig. S3 (see ESI‡) shows the TGA profiles of pristine SWCNT and *f*-SWCNT **1a** and **1b** prepared by method (ii). A loss of weight of around 12% for pristine SWNCT, 21% for **1a** and 27% for **1b** was observed at 650 °C. The loss of weight observed for pristine SWCNT between 100 and 650 °C may be due to the destruction of the residual amorphous carbon still



Scheme 1 Cycloaddition of benzyne to SWCNT.

f-SWCNT 1b

Table I Cisa	in ors core level spectra or f ow erver in and prismie of erver samples. In parenticises are peak percentages							
Sample	BE/eV (C1s (%))						BE/eV (O1s (%))	
	sp ² C	sp ³ C	C-0	C=O	COO	π-π*	0–C	0=C
SWCNT	284.8 (66)		286.2 (19)	287.7 (3.8)	289.2 (5.6)	291.4 (5.6)	533.5 (75)	532.2 (25
f-SWCNT 1a	284.8 (68)		286.2 (16)	287.7 (4.4)	289.2 (1.8)	291.4 (9.8)	533.8 (66)	532.2 (34

287.5 (5.7)

289.4 (3.8)

286.2 (19)

Table 1 C1s and O1s core-level spectra of f-SWCNT 1a, f-SWCNT 1b and pristine SWCNT samples. In parentheses are peak percentages

present in the carbon nanotubes and to the decarboxylation of the oxidized species. The corrected weight losses due to the functional groups on nanotubes (weight loss differences of 1a – pristine SWCNT and 1b – pristine SWNCT) were then estimated to be 9% and 15% for *f*-SWCNT 1a and 1b, respectively. The number of aromatic functional groups in *f*-SWCNT 1a was then estimated as 1 per 64 carbon atoms. Finally, the number of functional groups for *f*-SWCNT 1bcorresponds to one dialkoxy benzene group per 115 carbon atoms. The degree of functionalization for *f*-SWCNT 1aobtained by method (i) was estimated as 16% (1 benzene functional group per 35 carbon atoms).

285.4 (13.4)

284.8 (54)

X-Ray Photoelectron Spectroscopy (XPS) was used to identify the surface groups, the chemical state of the atoms, and their relative abundance in the functionalized SWCNTs.^{10,11} The high resolution C1s and O1s spectra of f-SWCNT 1a and 1b, and SWCNT samples are displayed in Fig. S4 (see ESI[‡]). The binding energies and peak assignments of C1s and O1s emissions are summarized in Table 1. Sample 1b was decomposed into five different components: (i) a major one placed at 284.8 eV (FWHM = 1.4 eV) originated from sp² C-atoms of the graphene sheets, together with its $\pi \to \pi^*$ shake-up transition at 291.4 eV,^{4,12} indicative of the presence of nanotube structures; (ii) a component at 285.4 eV (FWHM = 1.7 eV) assigned to the sp^3 C-atoms, namely from alkyl groups; (iii) a peak at 286.2 eV (FWHM = 1.8 eV) usually attributed to oxidized groups in C-O bonds;4,13 (iv) and (v) peaks located at 287.5 eV (FWHM = 1.9 eV) and 289.4 eV (FWHM = 2.2 eV) assigned, respectively, to C=O and COO groups.^{4,13} Sample *f*-SWCNT **1a** and SWCNT showed similar C1s line shape although the whole FWHM was about 0.2 eV smaller than for sample f-SWCNT 1b. Accordingly, C1s peaks of 1a and reference SWCNT samples were satisfactorily fitted using only four components (i, iii, iv and v) and the same FWHM values (see Fig. S4, ESI \ddagger) indicating the absence of sp³ C-atoms in both samples. The O1s peak (Fig. S4[‡]) showed a component placed at ca. 532.0 eV assigned to C=O surface groups whereas the second one at ca. 533.5 eV is associated to C-O groups in phenol-like structures.⁴ The surface atomic concentrations of the three samples are compiled as atomic percentages in Table S1 (see ESI[‡]). The pristine SWCNTs sample shows a considerable oxygen amount (7.6% total). The O-content drops drastically up to 1.8% for the benzynemodified f-SWCNT 1a sample, but increases again (6.5% total), as expected for the -OC₆H₁₃ chains linked to the benzyne structure during functionalization. In summary, detailed C1s fitting analysis pointed out the presence of sp² C-atom in the two benzyne-functionalized SWCNTs whereas only sp² C-atom is displayed by the pristine sample.

Raman spectroscopy is one of the preferred tools for the characterization of covalent functionalization of SWCNTs as

this technique gives information about additional structural defects disrupting the delocalized electron system in the SWCNT sidewalls.¹⁴ An increase in the I_D/I_G ratio is observed when the extent of SWCNT functionalization is increased. As depicted in Fig. 2, *f*-SWCNTs **1a** and **1b** exhibit an increase of the D-band (at around 1299 cm⁻¹) relative to the starting SWCNT, indicating a significant conversion of SWCNT sp² carbons to sp³ centers due to the functionalization in the walls of the tube.

291.4 (4.1)

533.5 (77)

531.9 (23)

A higher I_D/I_G ratio is observed in *f*-SWCNT **1a** (I_D/I_G = 0.30) compared to *f*-SWCNT **1b** (I_D/I_G = 0.21) suggesting a superior degree of sidewalls functionalization. Finally, it is important to remark that, as a SWCNT becomes functionalized, the electronic properties of the material change and the nanotube moves off resonance, and an apparent decrease in the intensity of the normally resonance enhanced RBM is observed.¹⁴

Cycloaddition of benzyne to SWCNT can form the [2+2] or [4+2] adducts (Fig. 3). It is well established that benzyne adds to naphthalene, anthracene and other PAHs forming the [4+2] cycloadducts.¹⁵ However, the reaction of benzyne with C₆₀ leads to the [2+2] adduct forming a cyclobutene ring.¹⁶ For the addition of benzyne to CNTs calculations suggest that

Fig. 2 (top) Raman spectra (785 nm, 1.58 eV) of SWCNT (black line), *f*-SWCNT **1a** (red line) and *f*-SWCNT **1b** (blue line), normalized at the G-band; (bottom) RBM region of SWCNT (black line), *f*-SWCNT **1a** (red line) and *f*-SWCNT **1b** (blue line).

Fig. 3 [2+2] (left) and [4+2] (right) products of the benzyne–SWCNT cycloaddition reaction.

both cycloadditions are possible, the [4+2] product being more stable than the [2+2] product, particularly in nanotubes with larger diameter than C₆₀ (0.683 nm).¹⁷ Consequently, it is important to determine the diameter of the SWCNTs employed in this work which can be done by analyzing the RBM zone of the Raman spectra¹⁷ (Fig. 2 (bottom)) by the application of relation (1):

$$\nu_{\rm RBM} \, (\rm cm^{-1}) = 248/\rm diameter \, (\rm nm). \tag{1}$$

The calculated diameters of our SWCNTs range from 0.88 to 1.49 nm (with laser of 1.58 eV, 785 nm) and from 0.79 to 1.77 nm (laser of 2.33 eV, 532 nm) (see ESI[‡], Fig. S5). So, according to ref. 2 and considering these diameters of CNTs, the [4+2] adduct is more stable than the [2+2] adduct and it should be the preferred product as indicated in Scheme 1. However, in a kinetic-controlled process this is only right if the difference of stabilities is present in the transition states.

Finally, further confirmation of the addition of the functional groups to the SWCNT is provided by Transmission Electron Microscopy (TEM), performed on samples before and after the functionalization procedure. In Fig. 4(A) we show a reference image with pristine nanotubes before any chemical procedure had been accomplished other than synthesis and purification of the nanotubes. SWCNTs are easily found in the image, where clean walls are visible. The average diameter of the pristine nanotubes is 2 ± 0.7 nm, where the uncertainty comes from TEM resolution. Some dispersion in diameters has also been observed. In Fig. 4(B) an image of a functionalized nanotube (f-SWCNT 1b) is presented, where the functionalization consists in the addition of dialkoxybenzene groups, the apparent diameter of this nanotube is slightly larger (4 \pm 0.7 nm), which can be explained by the uniform coverage of the original SWCNT wall. The dense functionalization seen by TEM is compatible with the high coverage predicted by the other characterization techniques presented in this article, which yields an addition of one

Fig. 4 Pristine (A) and functionalized (B) single wall carbon nanotube images obtained by TEM (200 kV, $250 000 \times$). Uniform coverage of dialkoxy-benzyne groups can be observed.

dialkoxy-benzyne group per 115 carbon atoms approximately. The nanotubes are stable while focusing the microscope image, but after some time under the electron beam current, some degradation can be appreciated in the nanotubes. The ESI‡ provides evidence of enough stability to provide good fixed images (see ESI‡, AVI-1 and AVI-2 movies).

In summary, we have demonstrated the viability of the cycloaddition of *o*-benzyne onto the sidewall of SWCNTs offering a new and powerful methodology to obtain functionalized carbon nanotubes. The construction of bigger wheels by reacting CNTs with polycyclic benzynes is in progress.

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