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Sidewall functionalization of single-walled carbon nanotubes through electrophilic addition†

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Electrophilic addition of chloroform to SWNTs followed by hydrolysis resulted in the addition of hydroxy groups to the surface of the nanotubes; further esterification with propionyl chloride led to the corresponding ester derivatives, which allowed us to identify their structure, also providing better solubility in organic solvents.

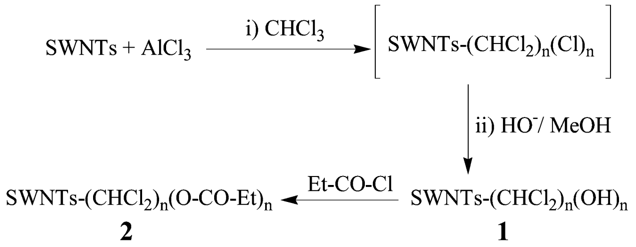
The study of chemical modification of carbon nanotubes at a molecular level is still at its infancy mainly due to their high insolubility in organic solvents. Derivatization through organic functionalization is, therefore, desirable as it improves both solubility and processability with the opportunity for fabricating novel nanostructures.[1,2]

To date, chemical functionalization of the side walls of carbon nanotubes involved direct fluorination and subsequent nucleophilic substitution,[3] addition of aryl radicals,[4] [2+1] cycloaddition of nitrenes,[5] addition of carbenes,[5] electrochemical reduction of aryl diazonium salts[6] and recently [1,3] dipolar cycloaddition of azomethine ylides,[7] as well as electrochemically reductive and oxidative coupling with phenylated derivatives.[8] Furthermore, chemical functionalization of defect sites especially located at the cap regions of the tubes has been reported.[9]

In this communication we report our results on the derivatization of SWNTs through electrophilic addition of $CHCl_3$ in the presence of $AlCl_3$. In addition, hydrolysis of the so-produced labile chlorinated intermediate species, and further coupling of the hydroxylated functionalized SWNTs **1** with propionyl chloride to the corresponding ester derivatives **2** (Scheme 1), not only gave information on their structures but, importantly, improved dramatically their solubility.

Electrophilic addition of polychloroalkanes to [60]-fullerenes has been previously reported with the simultaneous observation of alkyl-[60]-fullerenyl cation intermediates.[10] Moreover, pentaaryl-[60]-fullerene cations[11] as well as [76]-fullerene radical cationic species[12] have been prepared and characterized. However, electrophilic addition to carbon nanotubes has not been reported yet, though it would certainly be an intriguing reaction.

The initial stage of the functionalization process is based on the reaction of the SWNTs with chloroform in the presence of $AlCl_3$ (Scheme 1). We found that the solid state grinding of commercially available HipCO (purity of 95 wt% with Fe metal being the major impurity along with traces of amorphous carbon and carbon nanoparticles) SWNTs with the strong Lewis acid $AlCl_3$ facilitates the addition reaction most likely by initially producing thinner bundles of SWNTs from the pristine big ones.[13] This results in less compact bundles of nanotubes and, thus, renders the nanotubes more susceptible to reactions under the applied conditions. In a control experiment, simple heating or refluxing nanotubes in the presence of $CHCl_3$ and $AlCl_3$, but without mechanical grinding, resulted in the recovery of unreacted SWNTs. As shown in Scheme 1, under the conditions described in the experimental footnote,‡ one molecule of $CHCl_3$ would be attached to the surface of the nanotubes in the form of $CHCl_2$- and Cl-groups. The labile nature of this yellow-colored intermediate material did not allow its isolation and further characterization. However, after hydrolysis with alkaline methanol, in a one pot, two-step reaction (*cf.* Scheme 1), substitution of the labile Cl-atoms with HO-groups furnished functionalized nanotubes **1**.§ Further acylation with propionyl chloride transformed them into the corresponding ester-functionalized nanotubes **2** providing better solubility in organic solvents and, thus, allowing their structural characterization.



Scheme 1 Reaction scheme for the present functionalization of SWNTs.

Fig. 1 shows the IR spectra of the functionalized nanotubes (**1** and **2**) before and after acylation, respectively.

As is clearly evident, there is a broad absorption at 3370 cm^{-1} due to the free hydroxy groups for **1** (top spectrum) while for the ester derivatives **2** the characteristic stretching bands appear at 1725 cm^{-1} (C=O) and 1134 cm^{-1} (C–O) (bottom

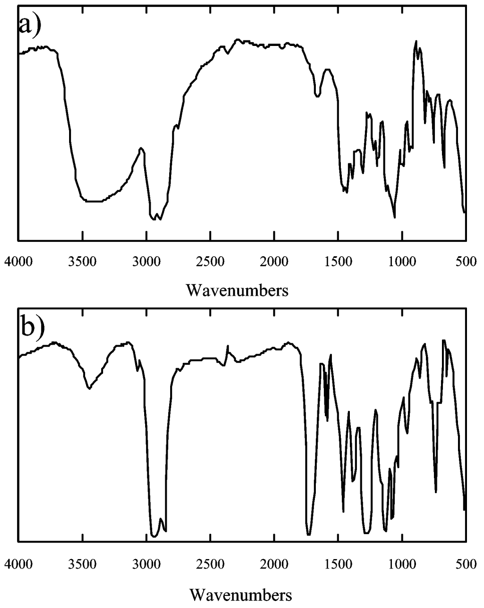


Fig. 1 IR spectra of functionalized SWNTs, a) compound **1** with free HO– groups on the surface and b) compound **2** with acylated HO– with propionyl chloride. The top spectrum clearly shows the HO– characteristic band while the bottom spectrum exhibits the –C=O band of the ester. FT-IR spectra were recorded using a KBr-DRIFT system.

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† Electronic supplementary information (ESI) available: Fig. S1: TEM views of functionalized nanotubes 1. Fig. S2: ^1H NMR spectrum of functionalized SWNTs 2 material. See http://www.rsc.org/suppdata/cc/b2/b204366a/

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spectrum). Also, absorptions due to the C–Cl stretching are present at 743 cm^{-1} while the bands at 2930 and 2852 cm^{-1} are due to the alkyl C–H stretching modes. There are more absorptions at around 1452, 1270 and 1063 cm^{-1} which can be attributed to the alkyl C—H and C—C bending modes and are slightly shifted and sharpened with respect to the ones for the derivative **1** before the acylation.

Transmission electron microscopy (TEM) was used to directly image the functionalized SWNTs **1** and **2**.¶ In Fig. 2, a TEM image of functionalized SWNTs **2** is presented. The image clearly shows the presence of SWNTs in the samples studied. Considerable differences can be found in the nature of the functionalized SWNTs before and after esterification (see ESI, Fig. S1, for images of functionalized SWNTs **1**). The solubility of the acylated SWNTs in organic solvents such as chloroform, dichloromethane and toluene has been substantially increased as a result of the numerous alkyl chains introduced to the nanotubes. Before acylation a large number of the hydrophilic free hydroxy groups in **1** promoted aggregation of the nanotubes in the form of thick bundles (left side image in Fig. S1). As soon as the esters **2** were formed, the solubility increased considerably which resulted in much clear images of thinner bundles of nanotubes (Fig. 2).

The absence of suitable protons together with the poor solubility of the polyhydroxylated functionalized carbon nanotubes **1** precluded further structural characterization *via* NMR spectroscopy. However, when the solubility was improved upon the introduction of the propyl alkyl chain as substituents of the ester moieties on **2**, we were able to measure its ^{1}H NMR in either chloroform or acetone deuterated solvents. From these measurements, the presence of protons introduced as part of the functional groups was identified, although these protons gave weak and broad signals. The latter can be explained by the statistical distribution of the functional groups on the nanotube surface as well as low symmetries of SWNTs. Furthermore, the rigidity in solution of this type of molecular materials equally contributes to the observed NMR results. The methyl and methylene protons of the propyl alkyl chains were, therefore, found to resonance as broad signals at 2.00–2.80 ppm, while the methine signals resonate at 4.70–4.90 ppm (see ESI, Fig. S2).

As described above, the esterification of an already functionalized SWNTs sample (*e.g.* **1** to **2**, *cf*. Scheme 1) clearly demonstrates that properly derivatized carbon nanotubes can behave as organic macromolecules. When free organic functional groups are present on their skeleton, common organic transformation reactions can occur. This opens the way to further derivatize and manipulate carbon nanotubes materials which surely provide numerous key intermediates for applications in diverse nano-technological fields.

Furthermore, future work on synthesizing such derivatized SWNTs bearing free functional groups will ultimately provide *carbon nanotube synthons* suitable for multi-step synthesis.

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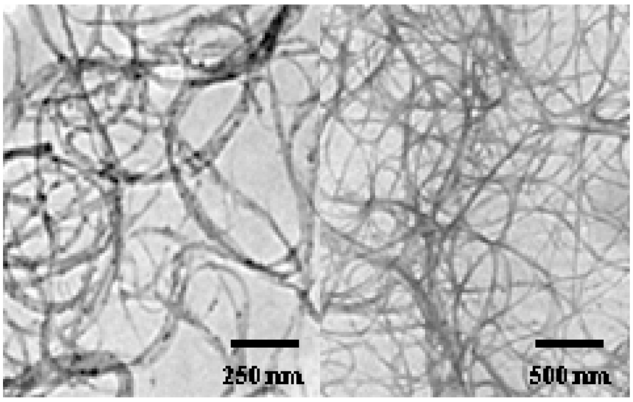

Fig. 2 TEM view of (a) pristine HipCO SWNTs (left side image), and (b) functionalized nanotubes **2** (right side image).

Notes and references

‡ A mixture of HipCO SWNTs and an excess of AlCl$_3$ was ground for 30 min in a mortar and pestle in a dry box. Then, the mixture was transferred in a round bottom flask filled with dry CHCl$_3$ and refluxed under argon for 48 h. Alkaline methanol was added to the yellow-colored reaction mixture and left under stirring for a further 20 h. After filtration, the solvents were evaporated to dryness to leave a solid residue that was repeatedly washed first with water and then with ether. For the acylation reaction, the solid functionalized SWNTs as previously obtained were suspended in propionyl chloride and the mixture was refluxed for a period of two days until dissolution was observed. The purified material was analyzed by IR and ^{1}H NMR spectroscopy as well as transmission electron microscopy.

§ It should be noted that some of the –Cl atoms in the addend groups of –CHCl$_2$ may also be substituted under the applied conditions. Therefore, Scheme 1 is a simplification of a more complicated situation that may happen.

¶ TEM examination of the products **1** and **2** was performed at an accelerating voltage of 100 kV. For the TEM (Philips 208) measurements, one drop of the sample suspended in hexane was placed on a copper TEM grid (3.00 mm, 200 mesh coated with Formvar film) and examined after air drying.

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