Rapid and controllable covalent functionalization of single-walled carbon nanotubes at room temperature†

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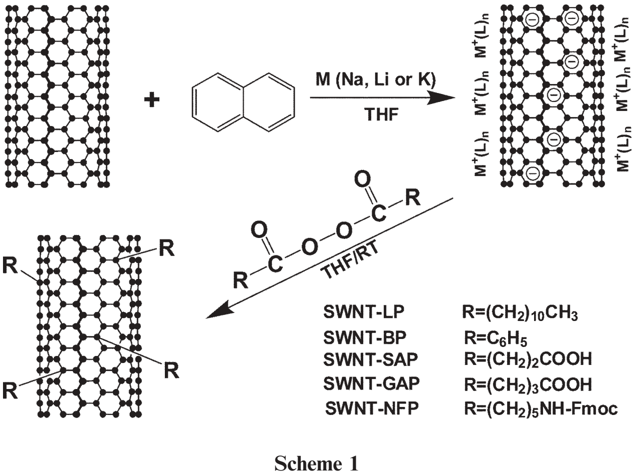
We report a rapid and efficient procedure to functionalize SWNT where free radicals generated at room temperature by a redox reaction between reduced SWNT and diacyl peroxide derivatives were covalently attached to the SWNT wall.

Single-walled carbon nanotubes (SWNT) exhibit the best mechanical, thermal and electrical properties of any known material. Combined with their very high aspect ratios that can reach well over 1000, SWNT is the dreamed material for the fabrication of composites with ultimate performance. Unfortunately, despite the wide availability of SWNT and despite many attempts, all SWNT-based composites reported to date showed poorer than expected performance, often worse than that of the pure matrices.[1] The main reasons for this are (1) highly variable purity and quality of the SWNT samples used, (2) poor dispersion/exfoliation and, (3) poor interface compatibility with the matrix. The second and third reasons are related to the intrinsic strong van der Waals interactions among the SWNT which lead to the formation of large bundles and to the intrinsic chemical stability of SWNT which makes binding to matrices rather difficult.

It is now widely accepted that chemistry is central to the development of high performance materials based on SWNT. Chemistry can solve the problems associated with bundles and the lack of binding with the matrices. In the past five years, side-walled covalent functionalization on neutral SWNT has received considerable attention, notably by the groups led by Prato,[2] Hirsch,[3] Tour,[4] Margrave,[5] Haddon,[6] and many others. Strategies to anchor all the practical functionalities have been developed. Two major drawbacks are that completion of the reaction at the single tube level requires substantial amounts of time and energy because the SWNT are inherently unreactive and bundled. The reaction proceeds on the outer tubes of the bundles first, which eventually exfoliate to expose the second layer to the reagents and so on. Reaction completion takes several hours, or even days, under refluxing conditions. As a result, chemical processing is the major and limiting cost associated with the integration of neutral SWNT in advanced materials. Chemical processing costs must be reduced to make industrial utilization of SWNT a reality. Recently, Penicaud *et al.*[7] showed that SWNT can be readily ex-foliated in standard solvents by reduction with an alkali metal though electron transfer mediated by alkali-metal–naphthalene–THF complexes. As the SWNT get charged negatively, they exfoliate as a result of electrostatic repulsion. This is an important practical advance because it readily allows chemistry at the single tube, thus saving a considerable amount of time. In addition, reduced tubes acquire higher nucleophilic character, thus allowing chemistry under less stringent conditions. Here, we show that reduced SWNT react readily within minutes at room temperature with diacyl peroxide derivatives to yield side-walled covalently functionalized SWNT. Furthermore, we show that the functionalization level can be controlled through repetitive action of the redox reaction.

Our approach is depicted in Scheme 1 and consists of directly adding an acyl peroxide derivative to a previously prepared suspension of reduced SWNT. Reduced SWNT can be prepared in one-step in either THF by electron transfer from alkali-naphthalene salts (ESI†) or in toluene by electron transfer from alkali-metal benzophenone salts. The acyl peroxide derivatives used here are terminated with alkyl, phenyl, carboxylic acid and Fmoc-protected amine functionalities, but the method should be applicable to any acyl peroxide derivatives so that in principle any functionality can be anchored on the SWNT at room temperature.

Similar alkyl, phenyl and carboxylic acid functionalization can be achieved with neutral SWNT but it requires the thermal activation (decomposition) of the peroxide derivatives and several hours, or even days, of reaction time.[8–10] Fmoc-protected amine



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details, Na content, XPS and Raman spectra of various samples, LC-ESI-MS of reaction byproducts. TGA results, MS-MALDI analysis, TEM images and photograph of SWNT-GAP suspension. See DOI: 10.1039/b712299c

functionalization of neutral SWNT through the thermal decomposition of the acyl peroxide derivative does not occur due to rapid radical–radical reactions (ESI†). Thus, it appears that our approach allows for new functionalizations, especially with amine terminated ligands. Reduced SWNT are obviously good reducing agents and hence are particularly reactive towards strong oxidizing agents such as peroxides, thus allowing the reaction to occur readily at room temperature. The limiting step is glassware handling rather than reaction kinetics.

The studies have been carried out with laser-grown materials prepared according to the two-laser method developed in our laboratory and reported previously.[11,12] The raw material has a purity estimated to 70–80% using a combination of characterization methods such as transmission electron (TEM) and scanning electron microscopy (SEM), Raman and optical spectroscopy, thermogravimetric analysis (TGA) and porosity measurements. Raman spectroscopy is a sensitive and useful tool to assess side-wall quality (graphitization) and side-wall functionalization. Our Raman characterization is done using the 514 nm argon-ion laser line with power density low enough for the Raman beam to be in the non-invasive mode, thus providing an accurate assessment of the wall structures. The 514 nm laser line excites mostly semiconducting tubes which form two-thirds of the total population of SWNT. The raw SWNT are purified to a purity of at least 90% through an in-house process that will be reported in detail elsewhere. The purification does not employ acid treatments but only flotation, sedimentation and extraction cycles that leave the side-wall intact, as determined through Raman spectroscopy (ESI†). All chemicals (reagent grade, 97–99%) were purchased from Aldrich except for $SOCl_2$ (Acros) and Fmoc-6-aminohexanoic acid (Genscript)

Fig. 1 shows the Raman spectra of pristine SWNT and SWNT-GAP samples. The reaction of reduced SWNT with glutaric acid acyl peroxide (GAP) leads to a substantial increase in the D-band intensity, indicating side-wall functionalization. This D-band increase is also correlated with an increase in the D + G combination mode at *ca.* 2925 cm^{-1}. The diameter distribution of the SWNT probed by the 514 laser line is very narrow as determined by a single radial breathing mode (RBMs) band at *ca.* 175 cm^{-1}. The relative intensity of the RBM remains unchanged upon functionalization. The figure also shows that the degree of functionalization can be increased (Fig. 1(C)), hence controlled, by repeating the redox process by reducing the previously functionalized SWNT (SWNT-GAP; Fig. 1(B)) and re-subjecting them to another reaction cycle with GAP. Similar data are obtained with the other acyl peroxide derivatives (ESI†). However, with GAP and SAP a higher degree of functionalization is achieved, as indicated by higher intensity in the D-band of the Raman spectra. This repetitive process also affords the possibility of anchoring functional groups of different types; one type per cycle, to produce multifunctional SWNT.

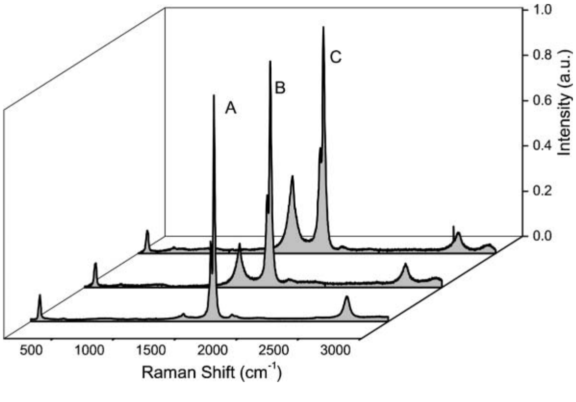

Fig. 1 Raman spectra of (A) pristine SWNT, (B) SWNT-GAP after the first reaction cycle, (C) SWNT-GAP after the second reaction cycle.

The degree of functionalization of carboxyl functionalized SWNT can be determined by first substituting the acidic proton with Na^+ using $NaHCO_3$ and then using microwave assisted acidic leaching of the sample in 3 M HNO_3 to free Na^+ for subsequent quantitation by ICP-AES (ESI†). The total concentration of Na in pristine SWNT (Fig. 1(A)) and SWNT-GAP after the first reaction cycle (Fig. 1(B)) was 3350, and 16500 ppm respectively, yielding a functionalization level of approximately 1C% after the first reaction cycle. A very similar value was obtained with TGA by measuring the mass loss upon heating. The $–CH_2CH_2CH_2COOH$ moiety desorbs at about 300 °C.

The identities of the functional groups anchored on the side-wall of SWNT have been ascertained by IR spectroscopy and XPS. Fig. 2 shows IR spectra of pristine SWNT, SWNT-GAP and SWNT-NFP samples. The feature near 1715 cm^{-1} in the spectrum of SWNT-GAP can be readily associated with the C=O stretching mode of the carboxyl acid moiety. In the case of SWNT-NFP, the feature associated with the carbonyl group of Fmoc appears at a lower frequency (1700 cm^{-1}), as expected. The bands in the 3000–2800 cm^{-1} region are attributed to the C–H stretching, whereas the features in the 1560–1550 region are due to C=C stretching mode activated by sidewall attachment.

Liquid chromatography electrospray ionization mass spectrometry (LC-ESI-MS) analysis of the filtrate from the reaction between reduced SWNT and NFP showed that the major byproducts of the reaction are Fmoc-6-aminohexanoic acid ($C_{21}H_{23}NO_4$), Fmoc-6-aminohexanoic acid methyl ester ($C_{22}H_{25}NO_4$) and two compounds ($C_{20}H_{21}NO_2$ and $C_{20}H_{23}NO_2$) formed by the disproportion of the Fmoc-5-aminopentyl radical (ESI†). The same byproducts were observed after the second functionalization cycle and when the SWNT and

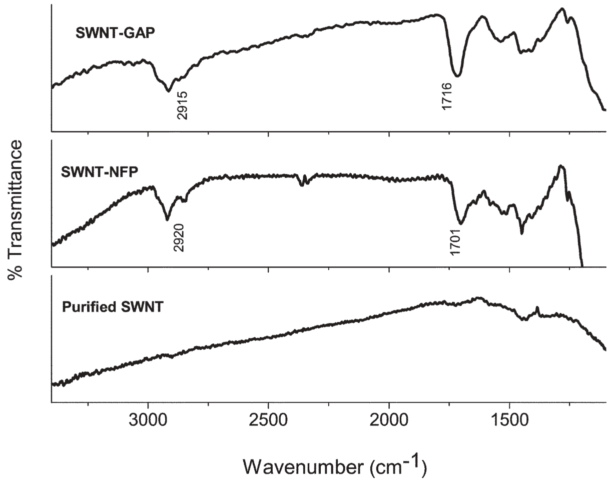

Fig. 2 Infrared spectra of pristine SWNT (bottom), SWNT-NFP (middle), and SWNT-GAP (top).

NFP were refluxed for a few hours in THF. These results are indicative of the radical pathway and also of the stability of the ligand under the reaction conditions. MS-MALDI analysis on SWNT-NFP confirmed that the anchored fragment is indeed –$(CH_2)_5$–NH–Fmoc (ESI†). The SWNT-NFP can be easily deprotected to reconstitute the primary amine for use in various applications.

In summary, a simple, efficient, and cost-effective method has been developed to functionalize SWNT at room temperature with useful functional groups. The process is amenable to practically any scales provided the reactions are carried out in oxygen-free environment, a condition regularly encountered in industrial settings.

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