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Sidewall functionalization of single-walled carbon nanotubes with organic peroxides†

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Single-wall carbon nanotubes (SWNTs) and their fluorinated derivatives (F-SWNTs) were reacted with organic peroxides including benzoyl and lauroyl peroxide to produce phenyl and undecyl sidewall functionalized SWNTs, respectively, which were characterized by Raman, FTIR, and UV-Vis-NIR spectra as well as TGA/MS, TGA/FTIR, and TEM data.

The sidewall chemical functionalization of single-wall carbon nanotubes (SWNTs) shows a great potential in improving their solubility for application processing, *e.g.*, in mechanically reinforced nanocomposites, and also in producing nanotube derivatives with altered electronic structures which can be tailored for specific useful properties.[1] However, the examples of the SWNTs sidewall derivatization chemistry[2] are limited. The radical additions studied involve only perfluoroalkyl and aryl radicals, produced photochemically or by electrochemical reduction, in contrast to a larger variety of known radical reactions of fullerenes.[3]

In this communication, we report the functionalization of SWNTs by covalent sidewall attachment of free radicals thermally generated from organic peroxides, such as lauroyl and benzoyl peroxides, commonly used as radical initiators in polymerization reactions.[4] Commercial availability of these peroxides as well as the ESR data showing the additon to C_{60} of radicals, produced by photolysis or thermolysis of some peroxides,[3] facilitated this work. Besides pristine SWNTs the same reactions were carried out on the fluorinated derivatives (F-SWNTs) (Scheme 1) to compare the reactivity of their corresponding polyaromatic and conjugated polyene π-systems toward radical addition. Both the solid-state and the solution phase reactions have been studied.

$$\text{(a) SWNTs + RC(O)OO(O)CR} \xrightarrow[-\ CO_2]{\text{heat}} \text{R-SWNTs}$$
$$\mathbf{1}\ \mathbf{a}\ R{=}C_6H_5;\ \mathbf{b}\ R{=}C_{11}H_{23}$$

$$\text{(b) F-SWNTs + RC(O)OO(O)CR} \xrightarrow[-\ CO_2]{\text{heat}} \text{F-SWNTs-R}$$
$$\mathbf{2}\ \mathbf{a}\ R{=}C_6H_5;\ \mathbf{b}\ R{=}C_{11}H_{23}$$

Scheme 1 Functionalization of carbon nanotubes (SWNTs and F-SWNTs) with benzoyl (R = phenyl) and lauroyl (R = undecyl) peroxides.

In these studies raw SWNTs, prepared by the HiPco process, have been thoroughly purified before further use to remove iron impurity as described previously.[5] The F-SWNTs have been prepared by direct fluorination of purified SWNTs to approximately C_2F stoichiometry according to the procedure published elsewhere.[6] Benzoyl peroxide was purchased from Fluka and lauroyl peroxide from Aldrich. For all reactions a 1 to 2 weight ratio of SWNTs material to peroxide was taken. In the solid state reactions a mechanically ground mixture of reactants was placed into a stainless steel reactor which was sealed and then heated at 200 °C for 12 h. The solution phase reactions were done by dispersing the SWNTs samples in *o*-dichlorobenzene by ultrasonication, adding the corresponding peroxide and refluxing the mixture under nitrogen at 80–100 °C for 3–120 h thereafter. The functionalized SWNTs **1**, **2** were isolated by washing off the unreacted peroxides and by-products with a large amount of chloroform on 0.2 μm pore size Teflon filter; the produced black film was peeled off and then dried in a vacuum oven at 100 °C overnight. The characterization of functionalized SWNTs **1**, **2** was performed by Raman, FTIR, and UV-Vis-NIR spectroscopy as well as TGA/MS, TGA/FTIR, and TEM data.

Raman and UV-Vis-NIR spectra showed clear evidence for the significant alteration of the electronic states of **1** and **2**. In the Raman spectra (see ESI†, Fig. S1) the observed decrease of the typical for purified HiPco-SWNTs breathing and tangential mode peaks at 200–263 and 1591 cm^{-1}, respectively, along with the substantial increase of the sp^3 carbon peak at 1291 cm^{-1} provide a diagnostic indication of disruption of the graphene π-bonded electronic structure of the side walls, suggesting their covalent functionalization. This is further confirmed by their solution-phase UV-Vis-NIR spectra (see ESI†, Fig. S2) which show typical for functionalized SWNTs[2] complete loss of the van Hove absorption band structures, routinely observed in purified HiPco-SWNTs.[5]

The FTIR spectra of the functionalized SWNTs, obtained by using the attenuated total reflectance (ATR) attachment, are shown on Fig. 1. The weak peaks in the 3060–3020 cm^{-1} range in the spectra of **1a**,**b** (shown under A and B, respectively) characterize the aromatic C–H stretches of phenyl groups attached to the SWNTs, while the peaks at 2919 and 2850 cm^{-1}, which appear after washing the reaction product with $CHCl_3$ followed by drying in a vacuum oven, belong to aliphatic C-H stretches. Several stronger absorptions in the 1600-1400 cm^{-1} can be attributed to phenyl ring stretches and a broad peak at 1105 cm^{-1} to the C-F stretch in **1b**. The attachment of long-chain undecyl groups to SWNTs and F-SWNTs is indicated in the spectra of **2a**,**b** (shown on Fig. 1 under C and D,

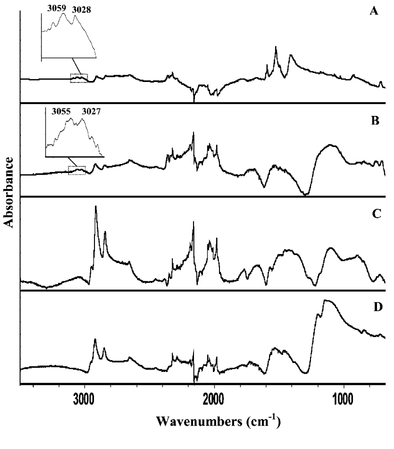

Fig. 1 ATR-FTIR spectra of functionalized SWNTs: (A) **1a**, (B) **1b**, (C) **2a**, (D) **2b**. The observed absorptions in the 1900–2400 cm^{-1} region are due to the diamond crystal of the ATR attachment.

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† Electronic supplementary information (ESI) available: Fig. S1: Raman spectra of pristine and functionalized SWNTs. Fig. S2: UV-Vis-NIR spectra of pristine and functionalized SWNTs. See http://www.rsc.org/suppdata/cc/b2/b209456h/

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respectively) by observation of prominent peaks of the C-H stretches in the 2980-2800 cm^{-1} range and an absorption of C-H deformation mode at 1465 cm^{-1}. In addition, a mid-intensity band at 1547 cm^{-1} and a doublet at 1202, 1145 cm^{-1} due to an activated C=C and a residual C-F stretches, respectively, are present in the spectra of **2b**. Based on the relative intensities of the C-H stretching modes in IR spectra of products **1**,**2**, it is reasonable to suggest that the radical additions to the F-SWNTs proceed more readily‡ which is in line with their stronger than pristine SWNTs electron accepting ability.

Further evidence for covalent functionalization of SWNTs has been provided by thermal degradation analyses (TGA) of **1, 2** in the 50–1000 °C range coupled with the on-line monitoring of volatile products either by MS or FTIR techniques. For instance, the TGA/MS data of **1a** (Fig. 2A) show the evolution of detaching phenyl radicals at 400 °C, indicated by a major peak on the *m*/*z* 77 and a smaller peak on the *m*/*z* 78 ion current *vs*. time plots (a) and (b), respectively, and their partial dimerization to biphenyl (*m*/*z* 154) volatizing at a higher temperature (plot (d)). These data confirm that the detected phenyl radicals originate from the functionalized SWNTs and not from the reaction by-products, such as biphenyl or benzoic acid ester $C_6H_5COOC_6H_5$, indicated by a very small peak on the *m*/*z* 105 plot (c). The TGA/FTIR analysis of another sample, **2b** (Fig. 2B), also shows on a derivative plot (b) a major peak at about 400 °C which corresponds to the loss of undecyl radicals by **2b**. This was concluded by synchronizing this peak with the maximum on the chemigram of the C–H stretch region (2800–2980 cm^{-1}) in FTIR spectra of volatile products (inset on Fig. 2B). Analysis of the same SWNT-derivative, **2b**, by variable temperature pyrolysis-EIMS confirmed the TGA/FTIR data by indicating the major loss of undecyl radical, $C_{11}H_{23}$, and their dimer at about 350–400 °C (peaks in EIMS at *m*/*z*155 and 310, respectively). It is important to note, that the thermal degradation of functionalized SWNTs results in formation of bare wall nanotubes, indicated by restoration of their features in the Raman spectra taken for solid residues after TGA analyses (see ESI,† Fig. S1).

The covalent attachment of a bulky long-chain group, such as undecyl, provided an opportunity to directly observe the functionalized SWNTs by TEM. Indeed, a high resolution TEM image of **2b** specimen (Fig. 3) clearly shows individual nanotubes with long-chain substituents joined to their sidewalls.

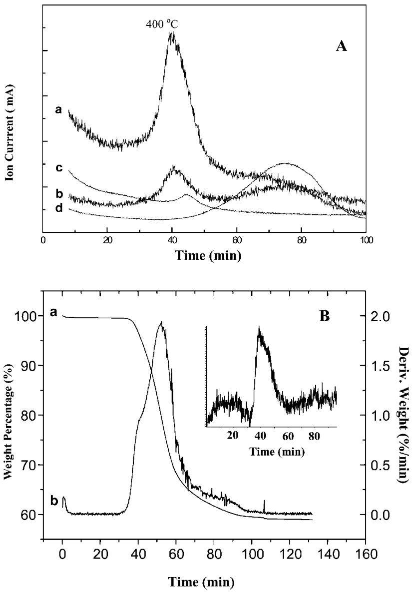

Fig. 2 (A) TGA/MS analysis of evolution products from **1a**. Ion current *vs*. time plots for *m*/*z* ions (a) 77, (b) 78, (c) 105, (d) 154. (B) TGA/FTIR data on **2b**. (a) Weight loss plot, (b) Derivative plot. Inset shows a synchronized chemigram of volatile products monitored by FTIR spectrum in the 2800–2980 cm^{-1} region.

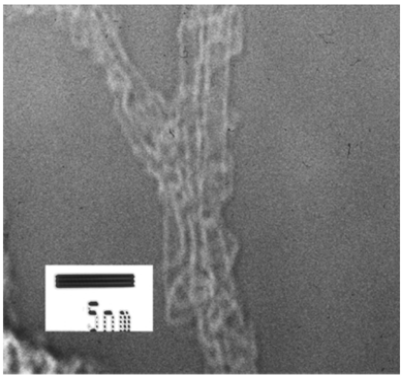

Fig. 3 High resolution TEM image of individual undecyl functionalized SWNTs, **2b**.

The reactions of benzoyl peroxide with the SWNTs and F-SWNTs were found to proceed more readily in the solid state, while functionalization using lauroyl peroxide has been efficient only in the solution phase. We observed the same reactions to go on much faster with the C_{60} and take only a few hours in comparison with several days required in case of pristine SWNTs, having significantly lower sidewall curvature. Nevertheless, the functionalization of nanotubes in the present work has been successfully done by a fairly simple approach with low cost, commercially available radical precursors. Besides using the free radicals produced by the thermal decomposition of peroxides to functionalize the SWNTs, we are currently investigating the possible crosslinking effects of this process which involve a larger number of organic peroxides and also the other carbon materials, *e.g.*, multi-walled carbon nanotubes, fullerenes, polyfullerenes, and graphite.

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Notes and references

‡ This is also indicated by a much shorter reaction time (3 h *vs.* 5 days) required in case of F-SWNTs for observation of prominent C–H peaks in the FTIR spectra of nanotube derivative **2b** in comparison with the SWNT-derived product **2a**.

1 C. N. R. Rao, B. C. Satishkumar, A. Govindaraj and M. Nath, *CHEMPHYSCHEM*, 2001, **2**, 78; B. Gao, G. Z. Yue, Q. Qiu, Y. Cheng, H. Shimodu, L. Fleming and O. Zhou, *Adv. Mater.*, 2001, **13**, 1770; *Carbon Nanotubes: Synthesis, Properties and Applications*, ed. M. Dresselhaus, G. Dresselhaus and Ph. Avouris, Springer-Verlag, Berlin, 2001.

2 J. L. Bahr and J. M. Tour, *J. Mater. Chem.*, 2002, **12**, 1952; V. N. Khabashesku, W. E. Billups and J. L. Margrave, *Acc. Chem. Res.*, 2002, **35**, 1087.

3 B. L. Tumanski, *Russ. Chem. Bull.*, 1996, **45**, 2267; M. Walbiner and H. Fischer, *J. Phys. Chem*, 1993, **97**, 4880; J. R. Morton, K. F. Preston, P. J. Krusic, S. A. Hill and E. Wasserman, *J. Phys. Chem.*, 1992, **96**, 3576.

4 *Organic Peroxides*, ed. D. Swern, Wiley-Interscience, New York, London, Sydney, Toronto, 1971, Vol. II, 799.

5 I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley and R. H. Hauge, *J. Phys. Chem. B*, 2001, **105**, 8297.

6 Z. Gu, H. Peng, R. H. Hauge, R. E. Smalley and J. L. Margrave, *Nano Lett.*, 2002, **2**, 1009.