

Chemical functionalization of carbon nanotubes with aryl diazonium salts

Anastasia A. Golosova,¹ Christine M. Papadakis¹ and Rainer Jordan^{1,2*}

¹ Wacker-Lehrstuhl für Makromolekulare Chemie, Department Chemie, TU München, Lichtenbergstr. 4, 85747 Garching, Germany.

² Professur für Makromolekulare Chemie, Department Chemie, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany.

ABSTRACT

We describe a facile and direct method for the functionalization of single-walled carbon nanotubes with 4'-substituted phenyls and biphenyls. By means of Raman spectroscopy and thermogravimetric analysis we demonstrate that a simple protocol of a direct chemical grafting in acetonitrile solution of the corresponding diazonium salts at room temperature results in a formation of stable aryl monolayers on carbon nanotubes.

INTRODUCTION

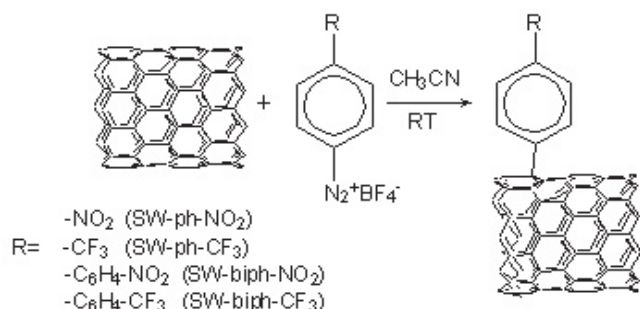
Carbon nanotubes (CNTs) have attracted much attention because of their mechanical, electrical, and thermal properties [1]. In spite of many attempts to exploit CNTs, e.g. as active fillers in a polymer matrix for obtaining composites with extraordinary characteristics, a number of challenges, e.g. the effective incorporation of CNTs within the surrounding matrix, are still unsolved.

Due to the strong van der Waals interactions, hydrophobic CNTs tend to organize into large aggregates, which behave differently from individual CNTs [2]. Moreover, being formed from graphene sheets, which are comprised of sp²-carbon, CNTs are very hydrophobic and almost inert to chemical modifications. Hence, a number of studies were devoted to improve the dispersibility and solubility of CNTs in solvents or in a polymer matrix by means of direct chemical modifications [3]. Among other modifiers, aryl diazonium salts proved to be useful and versatile reagents for a functionalization of the sp²-carbon with a variety of functional groups, and different reaction conditions have been proposed. Modification of small diameter (0.7 nm) single-walled carbon nanotubes (SWCNTs) was achieved via electrochemical reduction of aryl diazonium salts where the formation of reactive aryl radicals was triggered by electron transfer between CNT and aryl diazonium salt [4]. A similar reaction mechanism was suggested for thermal activated modification of SWCNTs with *in-situ* generated diazonium salts [5]. Later, Tour et al. [6] showed that the use of additional surfactants resulted in a significant improvement of the CNT functionalization because of the better dispersion of the native CNTs.

However, the main drawback of most modification reactions involving aryl diazonium salts is the well-known formation of multilayers of *p*-substituted aryls on the carbon surfaces, as e.g. observed for the electrochemical modification [7] or the reaction in aqueous media [8].

Recently, we reported on the formation of well-defined self-assembled monolayers of 4'-substituted biphenyls on ultrananocrystalline diamond by chemical grafting from a saturated solution of the aryl diazonium salt in acetonitrile at room temperature [9,10]. Herein, we report

on the application of this reaction for the chemical modification of single-walled (SW) and multi-walled (MW) CNTs (Scheme 1).



Scheme 1. Modification of CNTs with 4'-substituted (bi)phenyl-4-diazonium salts.

EXPERIMENT

In a typical experiment, 5–10 mg of native CNTs (SW-CNT received from BuckyUSA, MW-CNT “BayTubes” were received from Bayer AG, Leverkusen Germany as a generous gift) were dispersed in acetonitrile (*ca.* 0.03 wt %) by ultrasonication. To the dispersion, 0.15–0.5 equivalents of a 4'-substituted-4-diazonium salt (BF₄N₂-C₆H₄-R, [9,10]) were added and the reaction mixture was stirred for 5 days at room temperature. The obtained dispersion was filtered through a PTFE membrane (pore diameter: 0.45 μm) and washed several times with an excess amount of acetonitrile which effectively removed unreacted salt. The functionalized CNTs were dried under vacuum for one day at room temperature.

Characterization of the samples was performed by FT-Raman spectroscopy and thermogravimetric analysis (TGA).

RESULTS AND DISCUSSION

Native SW- or MW-CNTs were reacted with different 4'-substituted-4-diazonium salts (BF₄N₂-C₆H₄-R) at room temperature for approx. 5 days to allow completion of the reaction. After careful work-up and thorough washing of the CNTs all samples were analyzed by Raman spectroscopy.

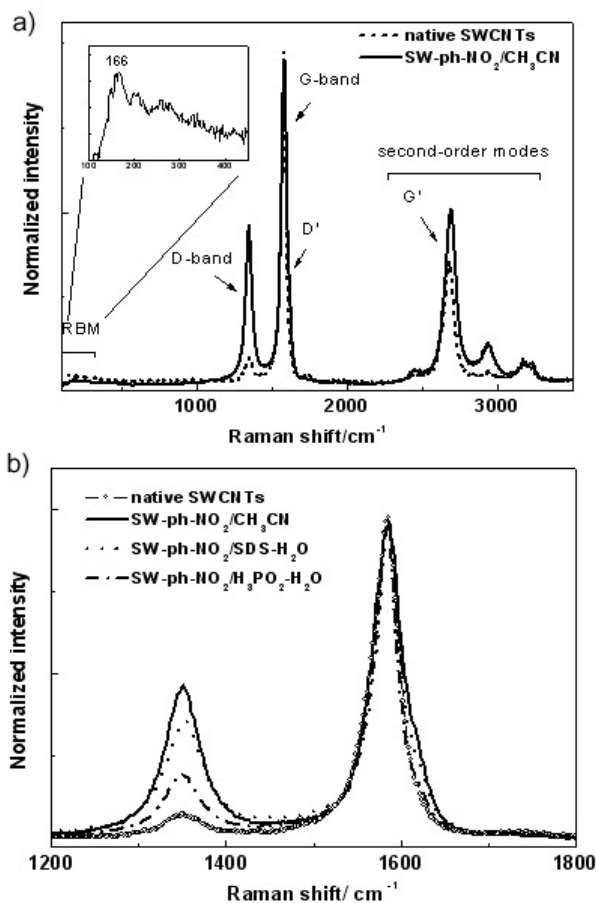


Figure 1. (a) Raman spectra (514 nm excitation) of native (dashed line) and modified with 4'-nitrophenyl-4-diazonium salt (solid line) SWCNTs (insert graphic gives RBM signatures); (b) First order Raman spectra for the SW-CNTs modified with 4'-nitrophenyl-4-diazonium salt by different techniques.

The Raman spectrum of native SW-CNTs (Fig. 1, dashed line) displays several signatures. The multiple peaks in the radial breathing mode (RBM) related to the low-frequency feature ($100\text{--}300\text{ cm}^{-1}$) are due to the distribution of tube diameters in the sample (insert of Fig. 1). On the base of the phenomenological relation between the Raman shift in the RBM region and the tube diameter [11], we estimate that the biggest fraction of SW-CNTs used in the present study had a diameter of around 1.45 nm. Disorder-induced (D) and tangential (G) spectral features are located around 1350 and 1585 cm^{-1} , respectively. The D-band originates from elastic scattering by defects in the CNT framework (sp^3 -carbons) and the intensity of G-band is associated with the amount of sp^2 -carbon. While for the native SW-CNTs the ratio (I_D/I_G) between the weak D-band and the intense G-band calculates to 0.08 and thus most of the carbon in the SW-CNTs are sp^2 -hybridized, (Fig. 1, solid line) the Raman spectrum changes significantly for SW-CNT after the reaction with the aryl diazonium salt. The main feature is the increase of the relative intensity of the D-band indicating the conversion of sp^2 -carbons to sp^3 state due to the covalent grafting of 4'-nitrophenyl onto the CNT framework. The I_D/I_G ratio changes significantly from 0.08 to 0.3. Besides the increase of the D-band, in the second-order spectra of the modified sample the signal at about 2930 cm^{-1} is enhanced while the intensity of the peak at 3170 cm^{-1} stays constant. For

the origin of the band at 2930 cm^{-1} , Fantini et al. [12] suggested the double-resonance mechanism, according to which this band must be assigned to a combination of the two defect-induced bands D and D' (at around 1620 cm^{-1} , overlapped with G-band). Thus, the enhancement of the feature at 2930 cm^{-1} also confirms the introduction of covalently bound functional groups to the CNT surface. To directly compare the results of this modification procedure with the previously reported methods, we performed modification of SWCNTs according to the protocols described for the reaction with diazonium salts with a surfactant (SDS) additive [6] (using 2.5 equivalents of salt for better comparison), and the reaction in hydrophosphorous acid/water solution [8]. Fig. 1b shows the obtained Raman spectra of the modified SWCNTs from each method. Taking the I_D/I_G ratio as a measure for the grafting efficiency, the modification using a saturated solution of aryl diazonium salts in acetonitrile resulted in the highest grafting ($I_D/I_G=0.3$) followed by the reaction with diazonium salts in SDS/water ($I_D/I_G=0.24$) and finally in hydrophosphorous acid/water solution ($I_D/I_G=0.16$).

The thermal stability of the native and modified SWCNTs is presented in Figure 2a.

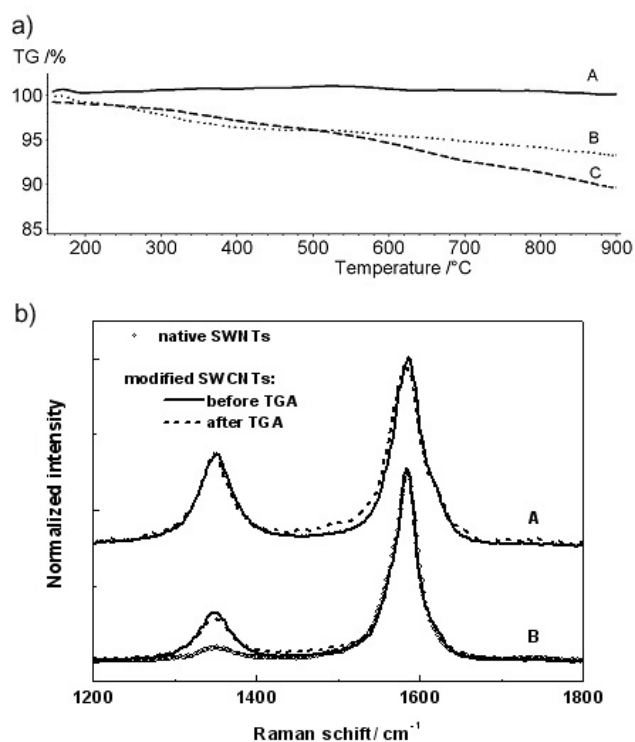


Figure 2. (a) TGA (Ar atmosphere) of SWCNTs: native (A), and modified with *p*-nitrophenyl (B) and *p*-trifluoromethyl-biphenyl (C); (b) Raman spectra before and after the TGA of SWCNTs modified with *p*-nitrophenyl (A) and *p*-trifluoromethyl-biphenyl (B).

While non-modified CNTs are stable up to $900\text{ }^{\circ}\text{C}$ (in argon atmosphere) with no significant mass change, SWCNTs modified with 4'-trifluoromethyl-1,1'-biphenyl or 4'-nitrophenyl show a weight loss of about 5–10 %. This is less than the expected values as reported in the literature for SWCNTs modified with aryldiazonium salts [4, 6] and indicates the formation of mono- instead of multilayers on the SWCNTs [7, 8] as previously observed for the

modification of diamond under the same reaction conditions [9]. Moreover, Haddon and coworkers [13] As indicated by the Raman spectra of the modified SWCNT the aryl ligands are bonded by a stable C-C-bonding onto an sp^2 -carbon framework. It is not likely that thermal decomposition selectively cleaves the aryl-CNT bond and desorption of the entire aryl moiety. The observed weight-loss should rather be attributed to the thermal desorption/decomposition involving the 4'-substitution. This is corroborated by the direct comparison of the TGA weight loss of phenyl and biphenyl ligands bonded onto the SWCNT which shows that approximately the same weight loss is observed for both modifications. To further confirm our assumption, Raman spectra of the modified CNTs before and after thermal treatment at 900°C (after the TGA analysis) were recorded (Fig. 2b). As apparent, the D-band intensity of the modified SWCNTs as well as the I_D/I_G ratio did not change upon heating indicating a stable C-C bonding of the aromatic units onto the CNT framework.

The change of the solubility/dispersibility of the modified SWCNT were preliminary investigated by their dispersion in a polar solvent such as water. In Fig. 3 the aqueous dispersions of native and 4'-nitrophenyl modified SWCNTs are depicted.

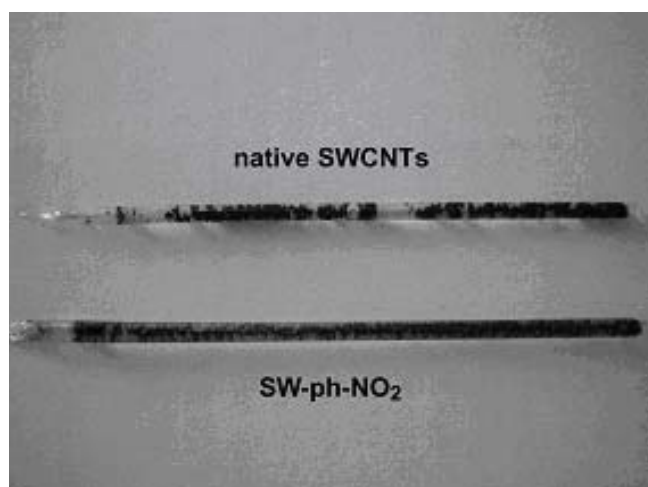


Figure 3. Aqueous dispersions of native and modified SWCNTs.

While native SWCNTs, being immersed into water, strongly agglomerate into big clusters (Fig. 3, top), the SWCNT covered with a polar nitro groups displayed an improved dispersibility (Fig. 3, bottom). However, the hydrophilicity of the modified CNTs is not too high as an aryl- NO_2 surface is only slightly hydrophilic with an advancing water contact angle of 64° as measured for a defined self-assembled monolayer [14]. Nevertheless, this straightforward experiment nicely shows the quite effective reduction of CNT agglomeration and changes of the CNT surface free energy because of the chemical modification.

CONCLUSIONS

In conclusion, the chemical modification of CNTs with (bi)phenyl diazonium salts results in the efficient and defined grafting of 4'-substituted phenyls and biphenyls onto carbon nanotubes. The formation of stable 4'-substituted aryl monolayers on the surface of CNTs have been investigated by means of Raman spectroscopy and TGA.

ACKNOWLEDGMENTS

We thank the International Graduate School of Science and Engineering (IGSSE) of the TU München and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

REFERENCES

1. Dresselhaus, M. S.; Dresselhaus, G.; Jorio, A. *Annu. Rev. Mater. Res.* **2004**, *3*, 247.
2. Schaefer, D. W.; Zhao, J.; Brown, J. M.; Anderson, D. P.; Tomlin, D. W. *Chem. Phys Lett.* **2003**, *375*, 369.
3. Burghard, M.; Balasubramanian, K. *Small* **2005**, *1*, 180.
4. a) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536.
5. Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, *13*, 3823.
6. Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *3*, 1215.
7. Kariuki, J. K.; McDermott, M. T. *Langmuir* **1999**, *15*, 6534.
8. Abiman, P.; Wildgoose, G. G.; Compton, R. G. *Int. J. Electrochem. Sci.* **2008**, *3*, 104.
9. Lud, S. Q.; Steenackers, M.; Jordan, R.; Bruno, P.; Gruen, D. M.; Feulner, P.; Garrido, J. A.; Stutzmann, M. *J. Am. Chem. Soc.* **2006**, *128*, 16884.
10. S. Q. Lud, S. Nepl, G. Richter, P. Bruno, D. M. Gruen, R. Jordan, P. Feulner, M. Stutzmann, J. A. Garrido, *Langmuir* **2010**, *26*, 15895.
11. a) Bachilo, S. M.; Strano, M. S.; Kittrell, C.; Hauge, R. H.; Smalley, R. E.; Weisman, R. B. *Science* **2002**, *298*, 2361; b) Sauvajol, J. L.; Anglaret, E.; Rols, S.; Alvarez, L. *Carbon* **2002**, *40*, 1697.
12. Fantini, C.; Pimenta, M. A.; Strano, M. S. *J. Phys. Chem. C* **2008**, *112*, 13150.
13. Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; De Heer, W. A.; Haddon, R. C., *J. Am. Chem. Soc.* **2009**, *131*, 1336.
14. a) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R.; Yang, G.; Liu, G. Y., *Langmuir* **2001**, *17*, 95. b) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R., *Langmuir* **1999**, *15*, 2095. c) Kang, J. F.; Ulman, A.; Jordan, R.; Kurth, D. G., *Langmuir* **1999**, *15*, 5555.