

## Raman spectroscopy on chemically functionalized carbon nanotubes

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We present Raman spectroscopy on carbon nanotubes, functionalized with alkyl groups to different degrees and with different addition reactions. We observe effects in particular on the intensities of the radial breathing mode (RBM). From the RBM we can assign the diameter and chiral indices of the tubes and study the influence of functionalization on different tubes, their transition energies, Raman shifts and RBM intensities. We observe a diameter dependence of the chemical reaction under certain reaction conditions.

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### 1 Introduction

Carbon nanotubes offer a wide range of amazing optical, electrical and mechanical properties [1]. Chemical functionalized nanotubes have come more and more into the focus in recent years, overcoming the problems of this carbon allotrope being quite unreactive and unsolvable. Functionalization is – generally spoken – the chance for a well-defined reaction of the tube to a special environment. For example, this could be the solubility in certain media [2]. Different types of functionalization have already been presented: endo- and exohedral, covalent and non-covalent [3].

Addition reactions have been established with various moieties. They all have in common fairly harsh reaction conditions to attack the tubes' sidewall [4].

Graupner et al. [5] reported an addition reaction sequence for the sidewall functionalization of single-walled carbon nanotubes (SWNT), in which the starting material is treated with tert-butyllithium. Afterwards a reoxidation of a t-Bu<sub>n</sub>SWNT<sup>n-</sup> intermediate state to an uncharged t-Bu<sub>n</sub>SWNT is done via bubbling oxygen through the dispersion. A preferred reaction of tert-butyllithium to metallic tubes has been reported, as it has been observed with other moieties like dichlorocarbene and diazonium salt [6, 7]. The higher reactivity of metallic tubes is commonly explained by their larger density of states at the Fermi level leading to the stabilization of transition states during the covalent attachment of an electron rich functional group to the nanotube [7]. Additionally the different reactivity has been explained by traditional chemistry concepts by Joselevich [8], stating the metallic species as less aromatic and having a smaller HOMO–LUMO gap. As a further effect on the reactivity Niyogi et al. [9] predict a diameter dependence of reactivity as a consequence of different pyramidalization and  $\pi$ -orbital misalignment

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angles in different carbon nanotubes. In this paper we present a comparison of two degrees of functionalization, the added molecules both being electron rich moieties.

## 2 Sample preparation

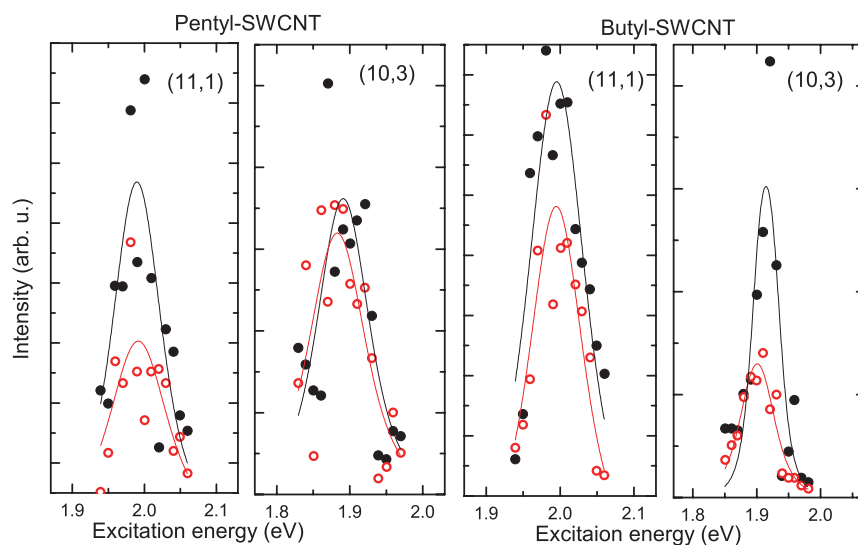
The starting material of all samples were obtained from Carbon Nanotechnologies Inc. (Purified HiPco® Single-Wall Carbon Nanotubes) and further purified by sonication and boiling in hydrochloric acid (37%). The procedure for the synthesis of (C<sub>5</sub>H<sub>11</sub>) SWNT was as follows: In a 250 ml nitrogen-purged and heat dried four-necked round bottom flask, equipped with sealed stirrer, gas inlet and pressure compensation and a septum, 100 ml of ammonia was condensed in an acetone-dry ice bath. 50 mg of purified HiPCO SWNTs and 0.5 g of sodium were added and stirred for two hours. To this solution 2.5 mL of 1 bromopentane were added slowly with a syringe through the septum. The mixture was then slowly heated to room temperature within 20 hours for boiling and evaporating the ammonia. The resulting grey solid was sonicated in a mixture of hexane and water, transferred in a separation funnel and purged with water and diluted hydrochloric acid until the pH-value remained neutral. The organic layer with the nanotubes was filtered through a 0.2 μm PTFE membrane filter and washed with ethanol and diethylether. The resulting black solid was dried in a vacuum oven at 50 °C overnight. The procedure for the synthesis of (C<sub>4</sub>H<sub>9</sub>) SWNT was: In a 250 ml nitrogen-purged and heat dried four-necked round bottom flask, equipped with two gas inlets and a pressure compensation, 20 mg of purified HiPCO SWNTs were dispersed in 100 ml anhydrous cyclohexane under sonication (15 min). To this dispersion 8 mL of tert-butylmagnesium chloride (1.7 M in THF) were added drop wise over a period of 10 minutes. After the completion of the addition the resulting suspension was stirred (30 min.) and sonicated (30 min.), resulting in a stable, black, homogeneous dispersion. The reaction mixture was stirred for 20 hours and subsequently quenched by bubbling oxygen for 30 minutes through the solution. The resulting heterogeneous dispersion was diluted with 100 ml cyclohexane, transferred in a separation funnel and purged with water and diluted hydrochloric acid until the pH-value remained neutral. The organic layer with the nanotubes was filtered through a 0.2 μm PP membrane filter and washed with cyclohexane, ethanol and water. The resulting black solid was dried in a vacuum oven at 50 °C overnight. In the pentyl sample, the amount of alkylated C atoms is 1.7% (TGA). The tert-butyl-SWCNT sample is probably of lower functionalization. For comparison two non-functionalized reference samples of the starting material were measured. For the resonant Raman measurements we used a micro-Raman setup in backscattering geometry, the sample was excited by a dye laser with a laser power of about 0.3 mW on the samples. The signal was detected by a charge-coupled device after analyzing the signal via a triple monochromator.

## 3 Results

We take the signal of the D mode at about 1300 cm<sup>-1</sup> in the Raman spectra as an indication of functionalization. For that reason we normalize the data to the second-order mode D\* [10], which is independent of the number of defects due to functionalization. The increase of the D mode, which is seen in the Raman spectra through a double-resonance process [11], is related to a successful addition reaction. We find an increase of the relative intensities  $D_{\text{functionalized}}/D_{\text{reference}}$  of 1.8 and 1.6 for pentyl and tert-butyl sample respectively, measuring the area under the peak confirming the addition reaction.

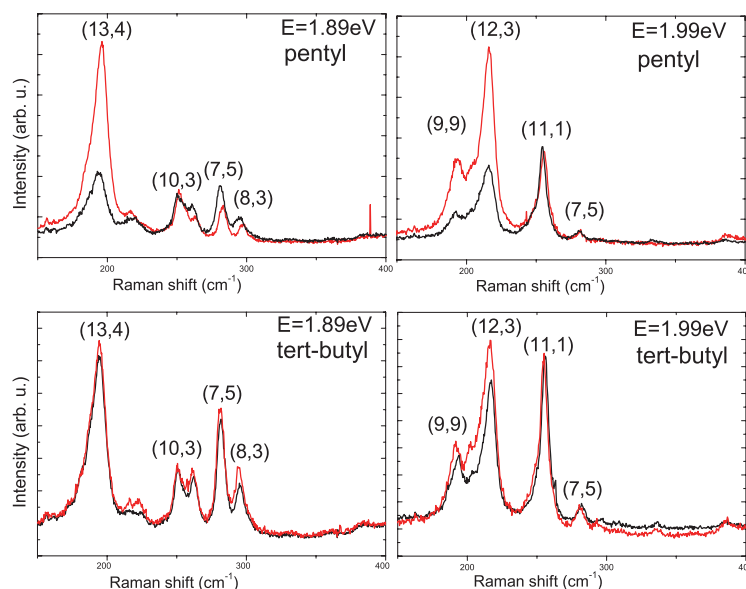
We find no significant shifts of the RBM peaks due to the addition reaction. The signal of the functionalized tubes seems to tend to higher energies, but only within the experimental accuracy of about 1 cm<sup>-1</sup>. We recorded full resonance profiles for (11,1) and (10,3) tubes, two nanotubes of same semiconducting branch. Bulk CaF<sub>2</sub> was used to normalize the signal intensity at different excitation energies. In Refs. [12, 13] the assignment of the chiral indices is described in detail. Concerning the transition energies we see a shift of the (10,3) tube of 8 (14) meV for the pentyl (tert-butyl) sample. For the (11,1) tube the shift is almost zero. The transition energies of all our samples are shifted about 60–70 meV to lower energies compared to isolated nanotubes probably due to the bundling of our nanotubes [14].

Comparing the RBM signal of the two functionalized samples we observe a remarkably different behavior for different tube diameters: In the samples with functionalization we see the maximum



**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Resonance profiles: functionalized samples (red open symbols) and reference samples (black symbols).

signal in resonance of semiconducting tubes with the exception of the (10,3) in pentyl-SWCNT significantly downsized (Fig. 1). In Fig. 2 we show RBM data of all four samples normalized to the signal of (11,1) and (10,3) tubes near their resonance. We did not observe a comparable decrease for the metallic tubes with larger diameter. The effect holds for almost all data points and is similarly pronounced for the whole range of excitation energies (2.06–1.83 eV). Even within the group of semiconducting tubes a diameter dependent effect seems pronounced comparing the intensities of (7,5) and (8,3) to (10,3) on top left of Fig. 2. Such a diameter dependence of reactivity is in agreement with Niyogi et al. [9].



**Fig. 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) RBM signal of pentyl (top) and tert-butyl (bottom) tubes normalized to (10,3) (left) and (11,1) (right) tube signal. Red: functionalized, black: reference sample.

In the tert-butyl samples we did not observe a comparably large difference between the tubes' signal. This can be understood on the basis of the different reaction sequences of our samples. Under the reaction conditions of the tert-butyl samples there seems to be no predominant effect on either tube species or certain diameters. The addition in general appears to be less pronounced, concerning the D mode intensity and the fact that we could not find additional lines in the spectra to be related to the added tert-butyl groups as we found for the pentyl samples [15]. For the pentyl samples the predominant dependence seems to be on diameter. However, additional effects on the addition of alkyl groups to carbon nanotubes cannot be ruled out. Further studies on small-diameter metallic and bigger diameter semiconducting tubes may show also effects concerning the tube species and a possible overlap of both effects. Chirality dependence is as well a promising field of investigation, especially having in mind the shift of transition energies as reported above.

#### 4 Summary

We showed the influence of chemical functionalization on the Raman signal of carbon nanotubes. From the Raman profiles of the RBM we found the strongest effect on the intensity of the radial breathing mode. The chemical reaction appears to be diameter selective under certain reaction conditions, possibly accompanied by an effect related to the tube species. Further work on the Raman intensities and the addition of different moieties and to different degrees is under way.

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