

# Diameter dependence of addition reactions to carbon nanotubes

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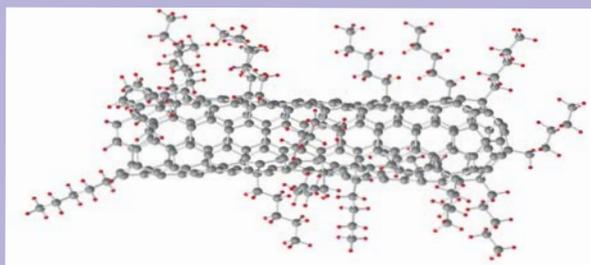
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We present resonant Raman measurements on carbon nanotubes functionalized with primary alkyl groups of different chain length. From the resonance profiles of the radial breathing mode (RBM) we assign the chiral indices of the tubes in order to study the selective reactivity of different tubes. We focus on diameter dependence showing inversely proportional behaviour to diameter for both metallic and semiconducting nanotubes.



Carbon nanotube, functionalized with pentyl groups, from phys. stat. sol. (RRL), 1, No. 4 (2007) coverpage.

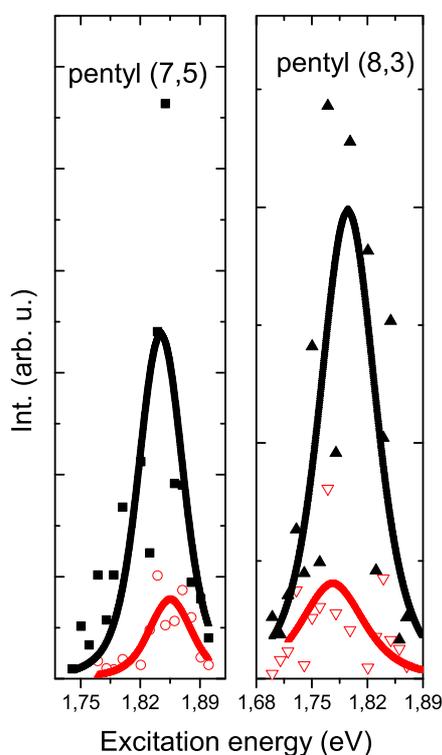
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**1 Introduction** Functionalization of single-walled carbon nanotubes (SWCNTs) by covalent bonding to the sidewall is among the most promising fields in carbon chemistry. It improves the handling of the tubes concerning their processability, e.g. the solubility is changed or they are combined with polymers in compound materials [1]. Its challenge is because of only a small slice of organic chemistry offering harsh enough conditions to attack the tubes [2]. Anyway, an increasing variety of reaction sequences has been established, even challenging reactions like [4+2] cycloadditions have been reported [3]. Selectivity of the reaction has been a hot topic right from the start. The major effects seem to be tube species and diameter. Higher reactivity of metallic tubes has been observed with various moieties [4,5], and well-established theoretical concepts do explain this convincingly [6,7]. Diameter dependence of the reactivity is because of different pyramidalization and  $\pi$ -orbital misalignment angles in different carbon nanotubes. That leads to higher local strain for tubes of smaller diameter that can be partially relaxed by sidewall addition [8]. This concept also reveals

the different chemistry of fullerenes and nanotubes [9]. Experimentally, Wunderlich *et al.* have recently shown these criteria for successful addition of organometallic compounds and also for the reductive alkylation to carbon nanotubes, showing the inversely proportional behaviour to the tube diameter. Additionally they report steric demands of the addends for the reactivity [10]. In this paper we show the diameter dependence of addition reactions, the added molecules both being electron rich moieties.

## 2 Sample preparation and experimental setup

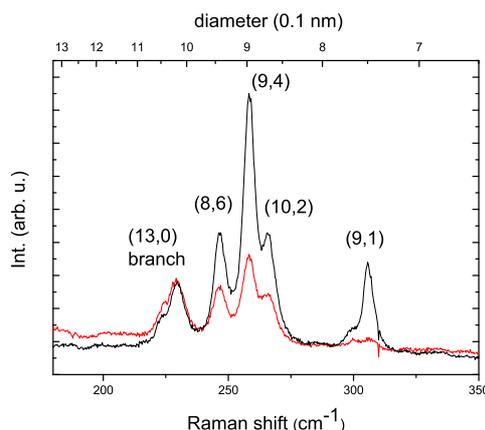
The starting material of our samples (Purified HiPco<sup>®</sup> Single-Wall Carbon Nanotubes) were obtained from Carbon Nanotechnologies Inc. and further purified by sonication and boiling in hydrochloric acid (37 %). For functionalization the tubes are dispersed in liquid ammonia by addition of sodium, then an alkyl halogenide is added. After evaporation of the ammonia ethanol is added. The heterogeneous dispersion formed in the end is purged with water until pH remains neutral, filtered, washed and dried to receive functionalized nanotubes in terms of bucky pa-



**Figure 1** Resonance profiles: functionalized samples (red open symbols) and reference samples (black symbols).

per. For the detailed procedure of synthesis of the different  $R_n$ -SWCNTs see [10]. The resonant Raman measurements were carried out using a micro-Raman setup in backscattering geometry, the samples being excited by a dye laser with about 0.3 mW laser power on the samples. A charge-coupled device is used to detect the signal after analyzing the signal via a triple monochromator. We recorded spectra of samples functionalized with different alkyl chains ( $C_5$  and  $C_{12}$ ) and spectra of the non-functionalized starting material for comparison.

**3 Results** We recorded full resonance profiles for various tubes and samples, here showing profiles of the sample with highest degree of functionalization as we see from the increase of the  $D$ -mode [11]. 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 [12]. Bulk  $CaF_2$  was used to normalize the intensities of the RBM signal at different excitation energies. A possible influence on the transition energies by functionalization is very small for our samples, especially compared to the full width at half



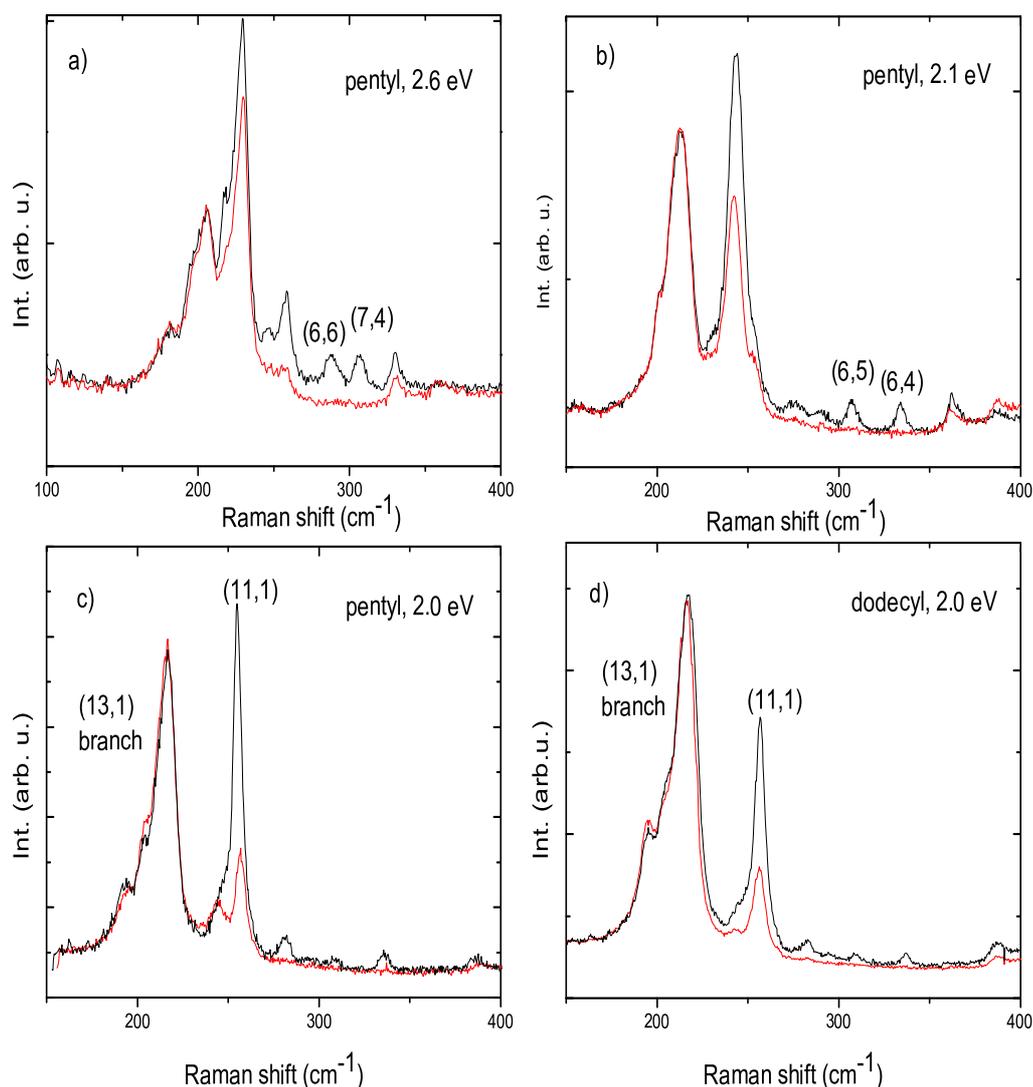
**Figure 2** Raman spectra of pentyl-SWCNT (red) and non-functionalized reference sample (black) at 724 nm excitation, probing various semiconducting tubes.

maximum of the profiles itself (see Fig. 1). This is important to show the effects of addition reactions to the sidewall on the RBM intensity. The remarkable decrease we see is not because the resonance window is left, but possibly due to effects on the electronic band structure, influencing the resonant Raman process by decreasing absorption strength [6]. Therefore the decrease of RBM intensity reveals a successful addition to a certain tube and is a viable feature to probe preferential functionalization of certain nanotubes. Our samples show a pronounced selectivity to diameter.

Figure 2 shows the general trend in the RBM intensities of the functionalized tubes that are decreasing with higher Raman frequencies, i.e., smaller diameter. The figure illustrates the inversely proportional relation between reactivity and diameter: in the bigger-diameter region around  $230\text{ cm}^{-1}$  the RBM signals of both functionalized and reference sample are of comparable intensity, the signals of the middle-diameter region ( $\approx 250\text{ cm}^{-1}$ ) are remarkably downsized and small-diameter signals around  $300\text{ cm}^{-1}$  are almost vanishing. It is worth pointing out that Fig. 2 shows semiconducting tubes only so that the downsizing can be attributed exclusively to the diameter effect in this case.

Comparing the different tube species reveals that the effect is present for both metallic and semiconducting tubes. One can see that both species generally display the same diameter-dependent behaviour, signal related to small-diameter tubes is almost vanishing with functionalization. It is obvious for small-diameter metallic tubes like (6,6) or (7,4), and also holds for small semiconducting tubes like (6,5) or (6,4) (see Figs. 3a, b). Chiral index assignment was done following the procedure of [13, 14].

For primary alkyl groups the chain length, as expected, does not significantly influence this behaviour. As shown in Figs. 3c and d, for different moieties the RBM intensi-



**Figure 3** RBM of functionalized samples (red) and reference samples (black) at different excitation energies. The signal is decreasing or even vanishing with higher frequencies for both metallic and semiconducting tubes (top) and holds for different chain length (bottom). The intensities are normalized to the very left band in the spectra.

ties show the same effect, quantitatively differences referring to slightly different degrees of functionalization. This holds for the whole range of excitation energies (roughly 1.7 - 2.6 eV). That shows the selective reactivity being inversely proportional to diameter is observable for both tube species as stated in previous work [15, 16]. Reaction conditions, sort of addend and degree of functionalization probably play a decisive role whether other effects like tube

species, moiety geometry, i.e., steric demands are becoming more or less predominant.

**4 Summary** We showed the diameter dependence of addition reactions to the sidewall of carbon nanotubes. We corroborate earlier results stating that the reactivity is selective and inversely proportional to the tube diameter. This can be observed for both metallic and semiconducting nan-

otubes. Other effects on the reactivity are probably collateral, but less dominant under given conditions and not issue of the present work. Further work on selective reactivity seems promising, because it may lead to both advanced nanotube application and an even deeper understanding of the intrinsic chemical properties of carbon nanotubes.

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