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New Strategies for the Chemical Characterization of Multi-Walled Carbon Nanotubes and their Derivatives

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Abstract

Industrially relevant characterization of multi-walled carbon nanotubes (MWCNT) is still remaining a challenging task. The aim of this work is to show novel and fast concepts for the chemical characterization of CNTs by combination of different analytical techniques. While the informations obtained by individual analytical tools like Fourier transform infrared spectroscopy (FTIR), attenuated total reflection infrared spectroscopy (ATR-FTIR), and Raman spectroscopy are not giving a full picture of the functionalisation of the MWCNTs, the combination of analytical tools such as FTIR or mass spectrometry with thermo gravimetric analysis are proven to be very useful methods for the chemical characterisation. Another focus of this contribution is put on sample preparation for FTIR and Raman spectroscopy, as this parameter shows a major influence on the obtained results. Suggestions for the sample preparation leading to results with high reproducibility are given. The measurements have been carried out on typical CNT samples such as commercially available pristine, carboxylated and amine functionalized MWCNTs, but also polystyrene (PS)-grafted MWCNTs. The results may serve as a guidance for the qualitative and quantitative characterization of CNT.

Keywords:

Raman Spectroscopy; FT-IR spectroscopy; TGA; Multi wall carbon nanotubes;

Introduction

The interest in carbon nanotubes (CNT) has exponentially increased ever since their (re)discovery at the beginning of the 90´s.[1-4] This is mainly due to their unusual electrical, thermal and mechanical properties.[1,2] The use of carbon nanotubes might open a new era in the design of supercapacitors and batteries, nanoscale sensors, electromechanical actuators, separation membranes, drug delivery systems or filled polymer composites.[2,3] For this reason the quality control of CNT materials and the employed CNT dispersions play a key role for an industrial application.[4-6] This means that the establishment of a fast and easy quality control method is essential for a successful product. The chemical (π-π conjugated system) and physical (high aspect ratio) structure of the carbon nanotubes leads to their principal advantages but also to their principal disadvantages, because these nanoparticles tend to remain highly aggregated and absorb electromagnetic waves across a wide spectrum.[7,8] It has been reported in several cases that the modification of the surface of the carbon nanotubes with functional groups can help to disperse them, and may lead to enhancement of mechanical properties and electrical conductivity in different matrices.[9-21]

In the case of the preparation of polymer nanocomposites based on carbon nanotubes, various researchers have reported an improvement of the mechanical properties when covalently surface-modified carbon nanotubes were used. Compared with non-covalently functionalized CNTs, covalently functionalized ones can interact directly with the matrix system as the polymer bound to the CNT can transfer stress directly from the matrix to the CNT structure.[9,14,17,22-28] However, the characterization of functionalized CNT is still difficult because of their high absorption of electromagnetic radiation across a broad spectrum [7,8]. This leads to a very low resolution for methods based on radiation like UV/Vis and IR spectroscopy. In consequence this circumstance leads most often to an inadequate characterization of the material if only one or a few different analytical tools are applied.[29,30,31] This situation is caused by the lack of a standard procedure of characterization and it is a big drawback for an industrial quality control.

If the surface functionalization between different types of carbon nanotubes is compared, the success of a covalent functionalization can be more easily analyzed when single wall carbon nanotubes (SWCNT) are considered. This is because changes on a single graphene layer can be better recognized compared to a superposition of graphene layers in multiwall carbon nanotubes

(MWCNT). In general, a covalent functionalization of a CNT π-system decreases the nanotubes conductivity and absorption against electromagnetic radiation or magnetic fields.[32-34] In addition, the alteration of a single layer of a π conjugated system decreases the electrical conductivity of CNTs. Looking at the possibilities offered by functionalized CNT, it is important to consider that the amount of SWCNTs produced is considerably lower than that of MWCNTs. For this reason, most of the efforts to incorporate carbon nanotubes into any mass production goods are put on MWCNTs. This means that most of the future industrially produced composites containing CNT will be based on unfunctionalized or functionalized MWCNT. Thus it becomes more and more important to improve the characterization strategies of MWCNT, which are more difficult to investigate as compared to SWCNT.

In this work we focus on Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and combinations of these methods – TGA-FTIR and simultaneous thermal analysis with mass spectrometry (STA-MS). All of these methods are commonly used in order to estimate the degree of functionalization, thermal stability and to reveal the nature of the functional groups.

Furthermore we use attenuated total reflection infrared spectroscopy (ATR-IR) in order to establish a fast and easy method for a qualitative measurement of functionalized samples. Instead of the commonly used ZnSe or diamond crystal, the ATR unit is equipped with a Ge-crystal, as the difference in refractive index between the carbon sample and germanium is larger than for the other commonly used materials for ATR-crystals.

Finally we discuss Raman spectroscopy and more specifically the effect of the shape of the sample surface on the resulting spectra. The use of mapping experiments leads to reliable statistically averaged values. Ultimately this investigation aims to establish a method for quality control of functionalized multiwall carbon nanotubes in large scale production.

Experimental

Materials

Multiwall carbon nanotubes (MWCNT) were synthesized and purified by FutureCarbon GmbH (Bayreuth, Germany, www.future-carbon.de) by a standard CVD and acid purification process, with a final carbon content that exceeds 98% (pristine MWCNTs). Amine functionalized MWCNTs (MWCNT-NH_2) were prepared using a diazotation reaction developed by FutureCarbon GmbH. The grafting of styrene from the MWCNT surface was done following a procedure described elsewhere [35], with a final polystyrene content of 15wt% (PS_{15}MWCNT) as determined by TGA. Before characterization, all samples were dried at 60 °C for 12 h to remove volatile solvents.

Methods

Fourier Transfer Infrared Spectroscopy (FTIR)

FTIR measurements were carried out on a Bruker Equinox 55 FTIR spectrometer (www.brukeroptics.com) with a DTGS detector and an aperture of 7.0 mm. 64 scans were taken in order to obtain a sufficient signal to noise ratio. Blackman-Harris-3-Term was used as the apodisation function for the Fourier-Transformation algorithm and a spectral resolution of 4 cm-1. The samples were diluted in potassium bromide powder (KBr) from Merck (www.merck.com) at a concentration of 0.1 wt%. 300 mg of the mixtures were pressed for 10 min at 10 t (Ø 1.3 cm) under vacuum, forming a grayish round disk.

Attenuated Total Reflection (ATR)

ATR-FTIR measurements were carried out using a Varian 670 IR Spektrometer equipped with a germanium (Ge) crystal (Pike Gladi ATR Ge-ATR). The powdered samples were fixed on the crystal with a powder sample-holder and were compressed to the surface of the crystal with a piston. 64 scans were taken at a spectral resolution of 8 cm-1.

Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) measurements were carried out using a Netzsch TG 209 F1 Iris (www.netzsch.com). The experiments were conducted under Ar flow (25 mL.min-1), from 35°C to 1000°C, at a constant heating rate of 5 K.min-1.

Thermal gravimetric Analysis (TGA) and FTIR measurements (TGA-FTIR)

TGA-FTIR coupled measurements were made using a Netzsch TG 209 coupled to the Bruker Equinox 55 FTIR spectrometer. Typical flow- and heating rates (25 mL.min-1 Ar, 35°C to 900°C, 10 K.min-1) were used.

Raman Microscopy

Raman spectra were recorded with a BrukerSenterra Raman Microscope equipped with a 532 nm laser and a 10 fold objective. Multiple sample areas were measured by applying a square array of 300 x 300 µm^2, where single measurements were taken every 30 µm. The result was evaluated by extracting each single spectrum and the areas related with the D and the G bands have been estimated by two Gaussian fits, using a home written routine. The A_D/A_G ratio has been calculated by fitting the curves between approx. 1684 cm-1 and 1448.5 cm-1 for the G mode and between approx. 1448.5 cm-1 and 1250 cm-1 for the D mode in the same way, respectively.
The disks prepared for the Raman measurement were prepared by pressing 100 mg of the CNT sample at 5 or 10 t (Ø 1.3 cm) for 5 to 15 min.

Results and Discussion

The quality and the chemical structure of CNTs have a primary impact on their properties and their dispersibility in a given medium. If MWCNTs are to be used on large scale, the necessity of an easy, fast, robust and relatively cheap characterization method of these nanoparticles is an important issue. In this sense, this paper starts with characterization methods that are of common use in a quality control laboratory and then combine some of these methods to better understand the chemical nature of the nanoparticles. The first choice is infrared spectroscopy, because it offers the possibility to recognize the functional groups present on the nanotubes. The study of the thermal stability of the nanoparticles gives information about the presence of adsorbed or covalently bonded chemical groups. A combination of the two methods helps to recognize the nature of the functional groups and the way they are bound to the CNT by analyzing the gaseous degradation products. The combination of thermogravimetry with mass spectroscopy leads additionally to the precise identification of the functional groups by their m/z value. Finally, with Raman spectroscopy information on the perturbation of the π-system from the changes in the ratio between the disorder (D) and the graphitic (G) mode of CNT is gained. The change in the D/G value provides information on an alteration of the CNT structure caused by a covalent functionalization.

IR Spectroscopy

Measuring FTIR of CNT with KBr pellets provides the possibility of varying the concentration of the sample. In contrast to ATR-FTIR with a common ZnSe/diamond crystal it is possible to obtain sufficiently low absorptions of the MWCNT sample, which leads to a narrowing of the peaks in the resulting FTIR spectra. Also the method can be easily adjusted to a given sample by varying the aperture for the beam and the CNT-concentration of the sample.

Fig. 1

FTIR spectra for various KBr/CNT ratios are shown in Fig. 1. The optimal result is obtained for a KBr pellet containing 0.1 wt% CNT. Using higher concentrations of CNT leads to too strong absorptions. The absorption of samples with higher concentrations of pristine MWCNT can be traced back to the defect free π-system of the sidewalls of the MWCNT. By recording spectra of a very diluted sample (0.1 wt% CNT) one is able to employ an additional baseline correction that allows the further evaluation of the FTIR data (see below).

After optimizing the concentration of pristine MWCNT we adapted these results to different functionalized MWCNT in order to prove the presence of specific absorption modes related to the functional groups (Fig. 2). Furthermore the strong absorption at higher MWCNT concentrations can be observed also for functionalized MWCNT due to the still unchanged inner walls.

Fig. 2

Fig. 2 shows an overview of the obtained FTIR spectra. Pristine MWCNT do not show noteworthy signals compared to the functionalized MWCNT.

Looking at the absorptions of the functionalized MWCNT and comparing them to spectra of similar molecules available from different data bases, correlations of the important sub spectra with the molecular structures expected from the reaction can be identified. All of the covalently functionalized MWCNT samples show signals which are typical for aromatic systems (900 – 1200 cm-1). They result from the destruction of the long-range π-system of the tube and the subsequent saturation of the opened bond with other species in the solution such as hydrogen. In the case of the oxidized MWCNTs the signals are better detectable because of the significant alteration of the sidewall with a high number of carboxylic groups. In the case of amine functionalization, analysis is more complex because of the presence of the benzene ring of the aniline, which is also visible in the spectrum. Another important signal for functionalized MWCNTs is observed in the alicyclic area between 2900 cm-1 to 3100 cm-1. In summary the FTIR spectra show aromatic signals, signals typical for aliphatic C-H-bonds and saturated rings resulting from covalent sidewall functionalization in addition to signals typical for the expected functional groups (also compare with the PS-grafted CNT in the ESM).

Fig. 3

ATR-FTIR, in comparison, does not offer the possibility of adjusting the absorption/reflection and in combination with the usual ZnSe/Diamond crystals this method leads only to baseline-like spectra. The reason for this is the low difference in the refractive index (diamond: n= 2.43, graphite: n = 2.15$\parallel$; 1.81$^{\perp}$ at 546 nm) [31] of unmodified MWCNT and the crystal, which leads to spectra of poorer quality than the ones shown in Fig. 1. To circumvent this problem, an ATR system with a germanium crystal (refractive index of Ge crystal: n = 4.00 at 546 nm; refractive index of ZnSe/Diamond: n = 2.41 at 546 nm) was used (Fig. 3). This difference in the refractive indices is sufficient to take ATR-FTIR-spectra of CNT powders and offers the possibility to carry out fast measurements (approx. 5 min.) of CNTs without the time consuming preparation of KBr pellets with CNT (approx. 20 to 30 min).

Thus FTIR and ATR-FTIR measurements can be considered as fast methods useful for industrial quality control during the synthesis and modification of CNTs. Especially the Ge-ATR-FTIR method combines fast analysis and easy handling even in cases of challenging samples like MWCNTs without compromising too much on sensitivity and spectral resolution.

FTIR provides information on the composition of the functional group and for example (see Figs. 2 and 3) the increase of the alicyclic signals caused by the introduction of the functional aniline group (Fig. 2 a) around 2800 cm-1.which gives a semi-quantitative information of the amount of a covalent sidewall functionalization. This is reasonable because these signals are related to the appearance of additional sp^3 hybridized C-atoms formed during the covalent functionalization.

While FTIR spectra of (MW/SW) CNT samples can give informations about the presence and amount of functional groups, typically no information about covalent or non-covalent binding of these functional groups is given.

Thermogravimetric Methods (TGA/TGA-IR/STA-MS)

TGA measurements have proven to be a useful tool to determine the amount of functional groups and to disitinguish between chemically bound and adsorbed functional groups on the surface of carbon nanoparticles. [29,30] Depending on the binding energies involved, the functional groups detach at different temperatures. Thus adsorbed groups will desorb from the surface at their boiling temperature or slightly above it, depending on the strength of the adsorption. The onset of the degradation of covalently bonded groups will be shifted to higher temperatures because the covalent bond between the CNT and the functional molecule has to be broken. For the TGA investigation of MWCNT and especially for functionalized MWCNT we chose a slow heating rate to differentiate between small amounts of chemically bonded and adsorbed functional groups on the surface. We focused on the onset temperature of the weight loss to estimate whether the detected weight loss is related to an adsorbed molecule or a covalently bonded one.

The first step of the TGA analysis is to compare the standard boiling temperature of the functional molecule (in our study: aniline), with the measured onset point of the weight loss of the functionalized MWCNTs. If the dissociation temperature of the functional group is known, one can determine the weight loss for each different group or molecule. Fig. 4 shows a typical heating trace from a TGA experiment with amine-functionalized MWCNT and will be used to discuss the common features of the TGA and TGA-IR measurements.

Fig. 4

The onset point of the two step weight loss is found around 212 °C (see Fig. 4), which is approximately 30 K higher than the boiling temperature of the related molecule (in our case aniline, Bp 184 °C). The beginning of this weight loss step (Fig. 4) might include some late evaporating molecules of adsorbed byproducts such as adsorbed aniline like structures, but the main part of the weight loss is related to covalently bound functional (aniline) groups.

The aniline group may be used for further postfunctionalisation reactions. Here we discuss some data of aniline functionalized MWCNTs, which were reacted with initiator groups for Atom Transfer Radical Polymersation, followed by a "grafting from" polymerization of styrene. The point of maximum weight loss (Fig. 4) in the first step is found at 290°C. This temperature is approximately 100°C higher than the boiling temperature of aniline. The maximum of the second weight loss (c) is found at 465°C.

From these TGA data it is evident that the maximum point of weight loss for most functional groups occurs at the higher decomposition temperature which indicates that they must have been covalently bonded. This two step weight loss of the functional groups has also been observed by Ellison et al. for amine functionalized SWCNT.[30]

The relevant quantitity for quality control is the degree of functionalization per gram of carbon on the surface of the MWCNT. It can be estimated by calculating the number of molecules decomposed during the measurement which is accessible through molecular weight, sample mass weight, mass loss, the number of walls and the diameter of the investigated tubes (an example of the calculation is shown in the ESM).

TGA is a strong tool for determining the amount of functional groups and thus the degree of functionalization. It depends on the previous analysis of the type and structure of the functional group in order to evaluate its amount. The result of the TGA measurement is the fast information about the degree of functionalization - if the chemical nature of the functional group is known. However, it is not possible to have a doubtless answer whether the detected weight loss is related to the signals observed in the previous FTIR measurements. Therefore a combination of TGA and FTIR can be used to establish a relation between the signals observed in FTIR and the weight loss measured with TGA.

The FTIR spectra collected from the gas phase (see Fig. 5) of the TGA/IR measurement show two signals in the alicyclic (2900 - 3100 cm-1) and in the aromatic (900 – 1200 cm-1) region of the spectrum. These signals are also present in the standard FTIR experiment (see Fig. 2) and can be related to aniline. Fig.5 shows that the maximum intensity of the IR signals is connected to the maximum gradient of weight loss in the TGA trace.

Fig. 5

The IR spectra in Fig. 5 show that both weight loss steps (with maxima at 292°C and 465°C) are caused by similar molecules that probably originate from the same functional group. An explanation of this fact is that there are two equal functional groups with different connections to the MWCNT. A closer look at a CNT shows that there are 3D (fullerene shaped end caps) and 2D (cylinder shaped sidewalls) deformed π-systems. In addition there are also groups on the sidewalls which are connected to defects in the CNT-structure such as 7-5-5-7 Stokes defects, kinks and others. Compared to an opening of a π-bond during the functionalization of the side wall the functionalization on defects and end caps breaks the tube forming σ-bonds. This explains the different thermal stability of the two types of connected similar functional molecules.

Considering the results of studies on annealing CNT [36-38] it appears that the π-system of a CNT is capable to self-regenerate which can be an explanation for the two different types of bonds with two different thermal stabilities. So the first step of the observed weight loss corresponds to groups connected through a bond with lower thermal stability and represents groups which have reacted with π-bonds. The second step represents groups which have opened end caps, Stokes-defects and other defect sites of the tube.

TGA-FTIR relates the weight loss detected in the TGA measurements to spectroscopic features of the outgoing group. It allows the identification of the decomposition products by comparing the spectra to gas phase spectra that are available in different databases.

TGA-FTIR is a rather simple coupled method and as such it is available in most quality control laboratories. It is possible to not only use this method during establishing a new synthetic route for stable product quality. Also for routine control during production of functionalized CNTs the permanent employment of TGA-FTIR is a powerful analytical tool.

Similar results can be obtained by a combination of simultaneous thermal analysis (STA) and mass spectroscopy (MS). More information on the STA-MS-measurements can be found in the ESM.

Raman spectroscopy

Raman spectroscopy has been widely used for the characterization of carbon nanotubes as well as other carbonaceous materials.[37] As for CNT, Raman spectroscopy gives information on the type of hybridization of the carbon atoms, the introduction of functional groups and chemical impurities, defects, nanotube diameter, the mass density, energy gaps, their metallic or semiconducting behavior.[38]

The characterization of multi-wall carbon nanotubes by Raman spectroscopy has been mainly focused on the comparison between the G band, which originates from the carbon-carbon bonds in-plane tangential and longitudinal stretching, and the D band, which is attributed to the presence of amorphous carbon or sp^3-defects in the graphene structure. The ratio between the areas of these two bands (A_D/A_G) has been used to quantify the degree of purification [40-42] or functionalization [43] of multi-wall carbon nanotubes. In some cases, however, it led to contradictory results.[44] The experimental setup of the Raman experiment might have an influence on the finally obtained spectrum. For example, increasing the laser power density leads to annealing of the structure defects of single-wall carbon nanotubes.[45]

Most studies employing Raman spectra of carbon nanotubes have been performed on one or only a few different locations on the sample surface of powder or buckypaper-like samples using standard Raman spectrometers. So often there are only a few spectra averaged leading to large standard deviation of the resulting D and G values.

Fig. 6

Fig. 6 shows Raman spectra of seven powder measurements of the same batch of pristine MWCNT from FutureCarbon GmbH placed on a common silicon waver which acts as a sample holder. The A_D/A_G values show a broad dispersion, which could be related to the inhomogeneity of the CNTs or to the preparation of the sample, especially the sample surface, for the Raman measurements. The latter could have a major influence on the quality of the spectra and might change the fitting of the areas corresponding to the G and the D modes. Therefore a new method of sample preparation was used. It consists of the preparation of a disk by "compression molding" (picture in the ESM) of the carbon nanotubes. The disks are smooth and safer and easier to handle compared to filling nanomaterials in a small cavity typically use as a sample holder.

The broad dispersion of results from different CNT samples of the same batch (Fig. 7) can be decreased by performing a statistical analysis of Raman spectra. The use of a carbon nanotube disk enables to run multiple measurements of one sample without causing changes of the structure of the material due to heating.[43] An example of multiple measurements (Raman mapping) is presented in the ESM. The results after the statistical analysis and the related standard deviation σ of 100 measuring locations are shown in Table 1.

Table 1: Comparison of the A_D/A_G value of pristine and functionalized MWCNT

Sample	**A_D/A_G**	**σ**
pristine MWCNT	1.3	0.3
MWCNT-COOH	1.2	0.1
MWCNT-NH_2	0.85	0.02

The A_D/A_G ratio of the pristine MWCNT is comparable to values reported in the literature.[35,36] Within the standard deviations, the acid treatment has a negligible influence on the mean A_D/A_G ratio compared to the pristine MWCNT. This confirms the assumption that the HNO_3 treatment at 65°C for 48h tends to remove the carbonaceous impurities in the MWCNT and destroys the residual catalyst, rather than affects the graphene structure of the MWCNTs. Thus Raman spectroscopy is not a conclusive method for the determination of the success of the purification or the inclusion of carboxylic groups on the MWCNT due to acid treatments. More aggressive acid treatment, however, leads to a severer destruction of the graphene-like structure of the carbon nanotubes.[39] In the case of MWCNT-NH_2 the A_D/A_G ratio is remarkably lower in comparison to the other two samples. This decrease might indicate that the diazotation reaction takes place not just on the MWCNT but also on the carbonaceous impurities present on the starting materials. This increases their solubility leads to the later removal by filtration of the reaction product. In this way the final product has a lower concentration of impurities compared to the pristine MWCNT. The marked decrease in the standard deviation also indicates the better homogeneity of the final product compared with the pristine and the acid treated MWCNT.

This seems to be an antagonism, but as the reaction is carried out under an excess of reactants there are enough reactive diazonium ions in the reaction medium to functionalize the outer wall of the MWCNT as well as the impurities. The impurities are then dissolved after their functionalization.

Moreover there is an increase of sp^2 hybridized carbon atoms introduced from the benzene ring of the functional amine group, which also should be taken into account for the decrease of the A_D/A_G ratio.

The advantage in using Raman mapping compared to conventional Raman measurements is that the resulting spectra originate from small individual spots and not from an average over a large sample area. This allows a better evaluation of the CNT quality (especially homogeneity) of the sample.

Conclusions

The results of the analytical measurements show clearly that no “stand alone” method can give complete information about the chemical composition of functionalized MWCNT by itself. This means that a fast and accurate analysis of CNT materials, especially for industrial quality management, can only be realized with a suitable combination of two or more methods, like TGA-FTIR or TGA-FTIR-MS. Without such combinations new synthetic routes or production schemes are difficult to be established. Further it is possible with such a combination of methods to measure samples parallel to the production process, which is much more efficient compared to the use of two to three single methods.

It is also shown that ATR-IR with a Ge-crystal can be used for the characterization of CNT to have a fast and brief look on functionalized samples and therefore this method is of high significance for further studies.

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Figures:

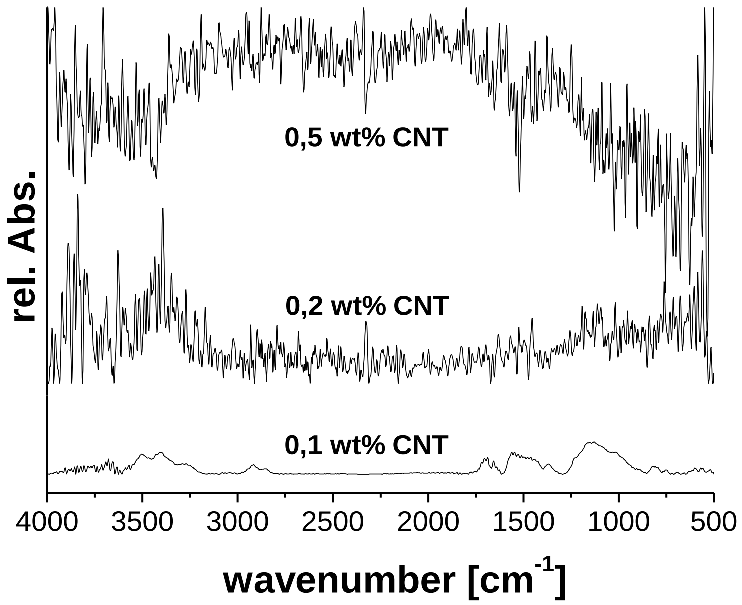


Fig. 1 Comparison of different pristine CNT contents in KBr for FTIR-spectroscopy; the different spectra were scaled separately for a better comparison

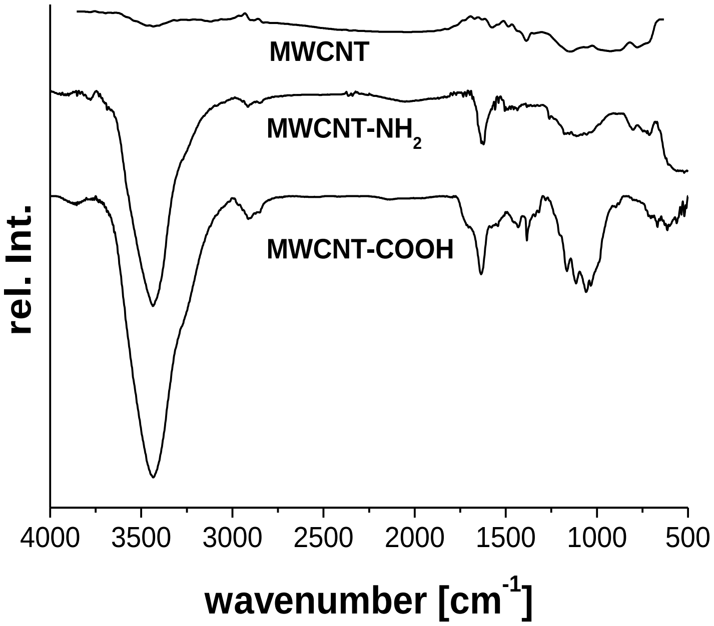


Fig. 2 Comparison of functionalized MWCNT; a) pristine, amine functionalized and carboxylated MWCNT; b) pristine, amine functionalized and grafted MWCNT; different spectra were adjusted for better comparison

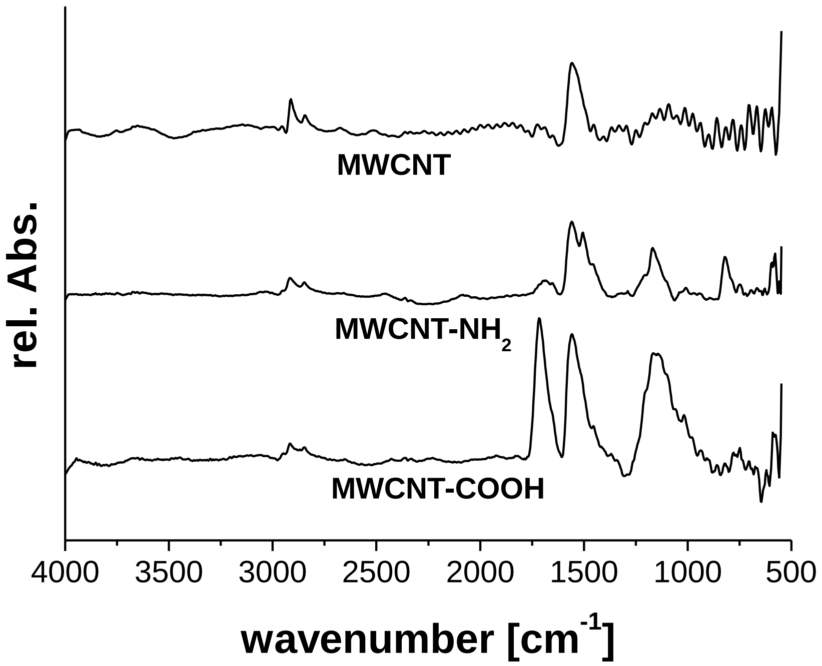


Fig. 3 ATR-FTIR spectra of pristine and functionalized MWCNT with a germanium ATR-crystal; different spectra were adjusted for better comparison

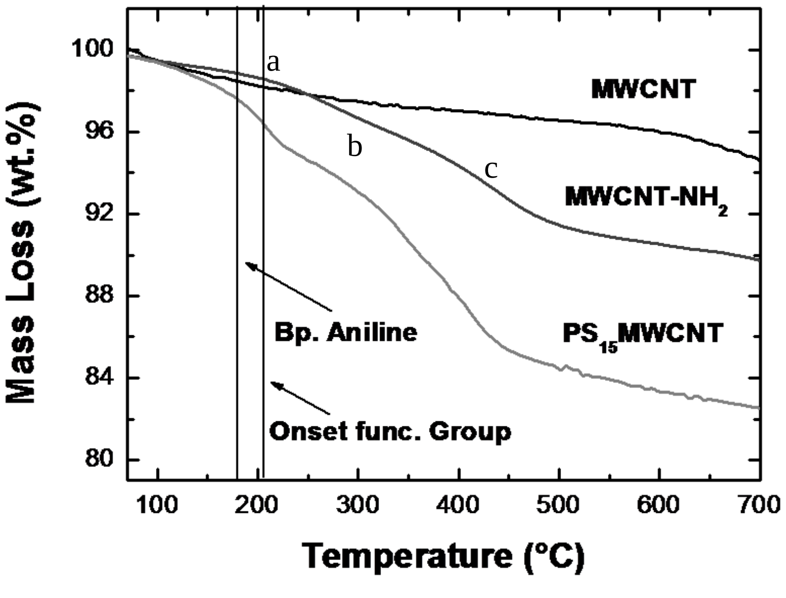


Fig. 4 TGA measurement of pristine and functionalized MWCNT

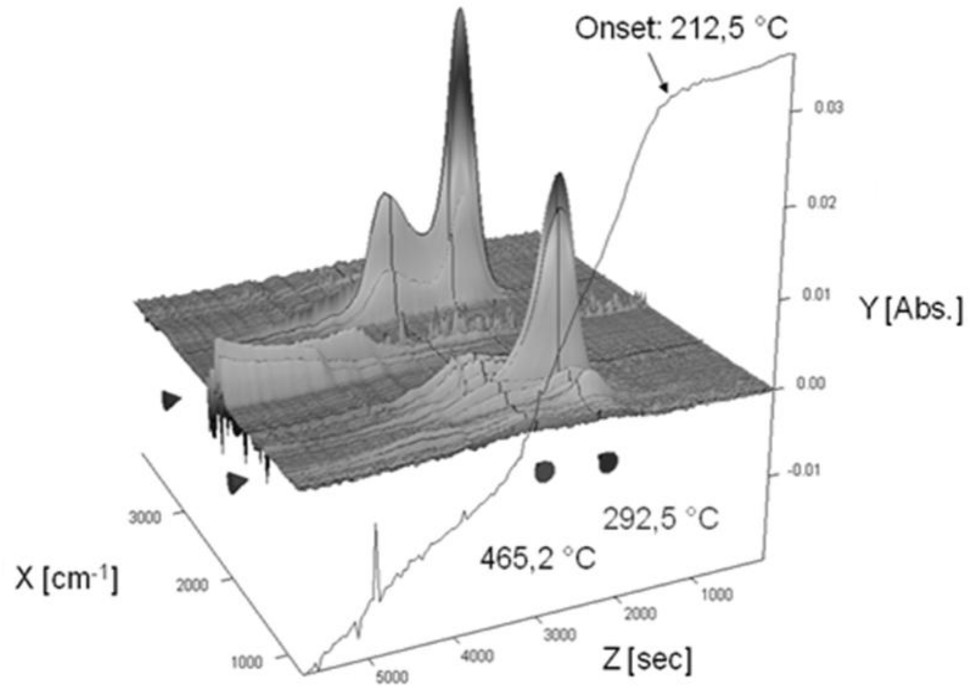


Fig. 5 3D-TGA-FTIR image of amine functionalized MWCNT with relating TGA curve

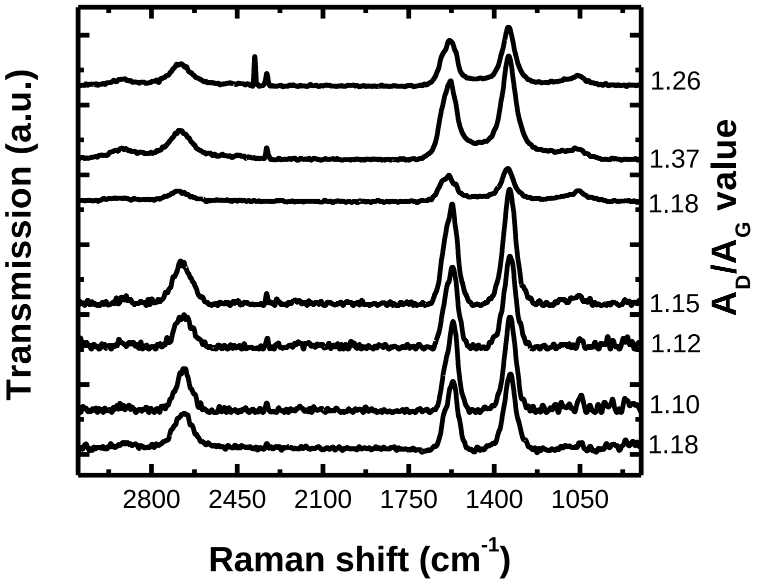
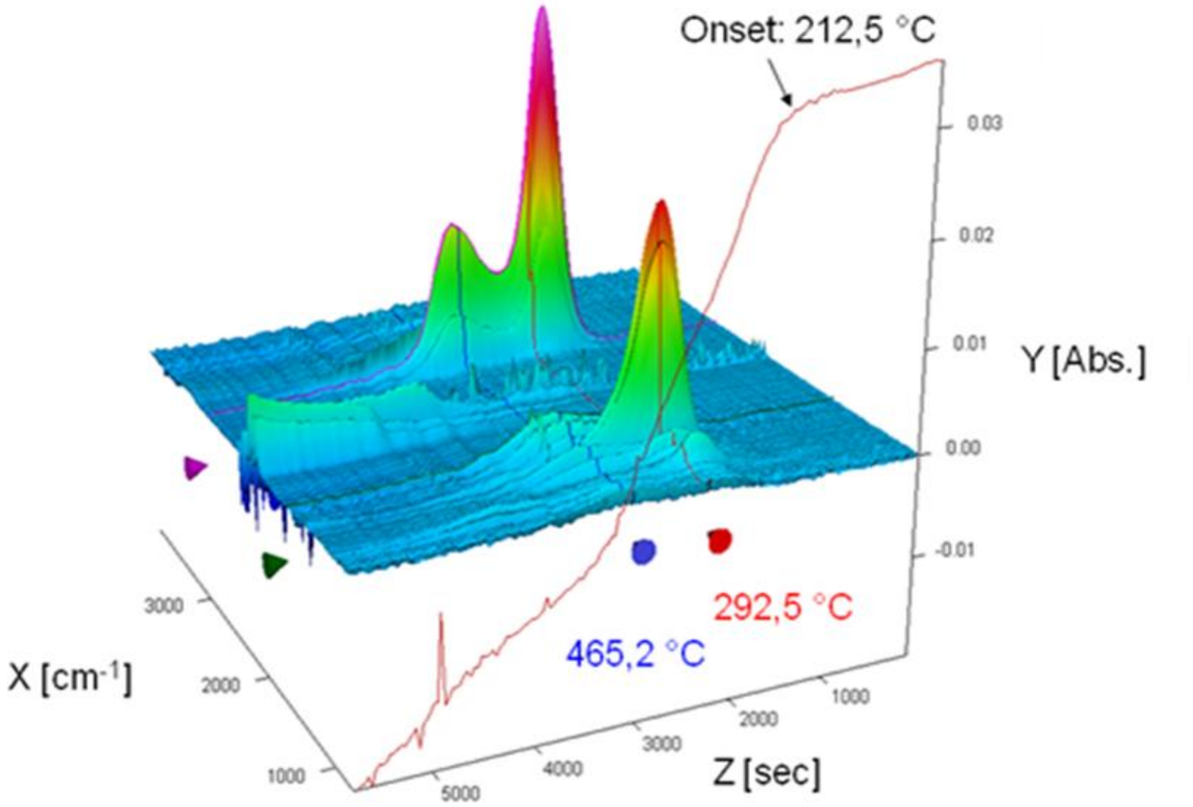


Fig. 6 Raman spectra of different powder measurements from exemplar pristine MWCNT-FC sample; different spectra were adjusted for better comparison

*Graphical Abstract



ESM

Example calculation of the degree of functionalization:

Tab. 1 Important values for the calculation of the degree of functionaliation (DoF)

Initial Weight MWCNT-R-NH$_2$-Powder:	**6,04**	**[mg]**
Weight Loss TGA (ref. to Initial Weight):	**9,96**	**[%]**
m/z-value of the functional aniline group:	**93**	**[g/mol]**
DoF drawn to 1g of sample:	**1,07**	**[mmol/g]**

$$6{,}04 \cdot 10^{-3}\, g \cdot 0{,}0996 \Big/ 93\, {}^{g}\!/\!_{mol} = 0{,}0065 \cdot 10^{-3} = 0{,}0065\, mmol$$

$$0{,}0065\, mmol \cdot \left(1000\, {}^{mg}\!\Big/\!_{6{,}04\, mg} \right) = 1{,}07\, {}^{mmol}\!\Big/\!_{g\ sample}$$

Simultaneous Thermal Analysis and Mass Spectroscopy measurements (STA-MS)

Experimental

The STA-MS measurements were carried out using a Netzsch STA 449 C and a QMS 403 C, operated under N$_2$ flow (25 mL.min-1), heating from 30°C to 1000 °C at a constant rate of 10 K.min-1.

Results

A second way to analyze functional groups with a known decomposition pattern in mass spectrometry leads to STA-MS combinations that provide a precise detection of the outgoing groups by measuring their characteristic m/z values. The example shows a measurement for amine-functionalized MWCNT, since this type of functionalization can be characterized more clearly by MS than oxidized or "grafted" ones. In case of MWCNT-COOH the oxygen functionalities decompose the tube during the measurement and PS-grafting of MWCNT leads to an unknown decomposition pattern. In addition the detaching temperature of the primary amine molecules is lower and better to evaluate compared to the decomposition products of the acid groups (CO_2 and H_2O).

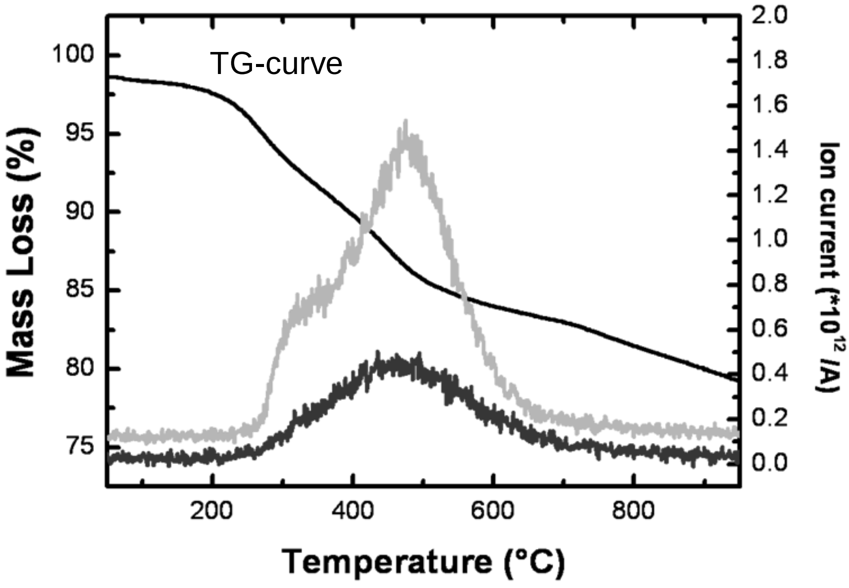


Fig. I STA-MS spectra of MWCNT-NH_2; gray: m/z = 93, dark grey: m/z = 94

As an example, Fig. I shows an STA-MS-measurement of amine-functionalized MWCNT. It also shows the two-step degradation already observed in the TGA results: One for the functional groups at the sidewalls and one for the groups on the end caps (compare TGA-FTIR results). The shown MS curves (grey and dark grey curves) relating to the m/z values 93 and 94 are typical for the molecule, in this case aniline (referred to the NIST data base).[36] The point of maximum degradation is comparable to the results of the TGA-FTIR measurements.

This method can give direct correlation between the type of the functional group and the point in time at a given temperature where it is decomposing from the MWCNT. It provides a good overview of the product and is fast and easy to handle which is of importance for industrial quality control.

Further FT-IR-Measurements on PS-grafted MWCNT

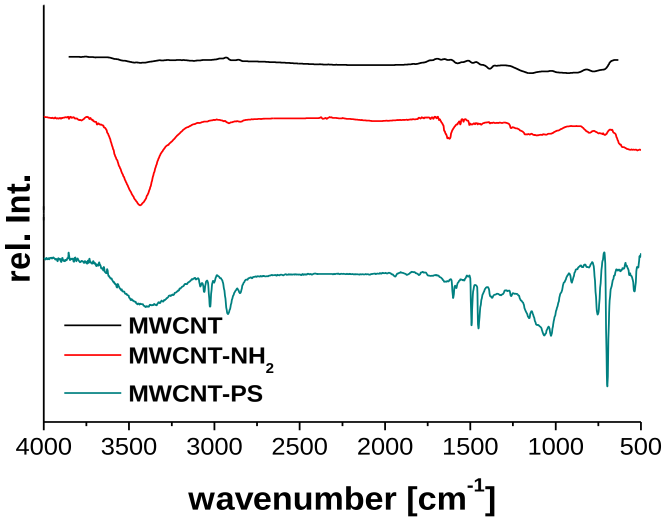


Fig. II: Comparison of different pristine, amine functionalized and grafted MWCNT; different spectra were adjusted for better comparison

The comparison of the spectra shown in fig. II shows the results of a strait forward functionalization, starting with pristine MWCNT followed by a diazotation with p-Phenylenediamine and a final ATRP-Polymerization. After the adjustment of the measurement parameters for FT-IR it was possible to monitor the process step by step.

2D-image of TGA-FTIR Measurements

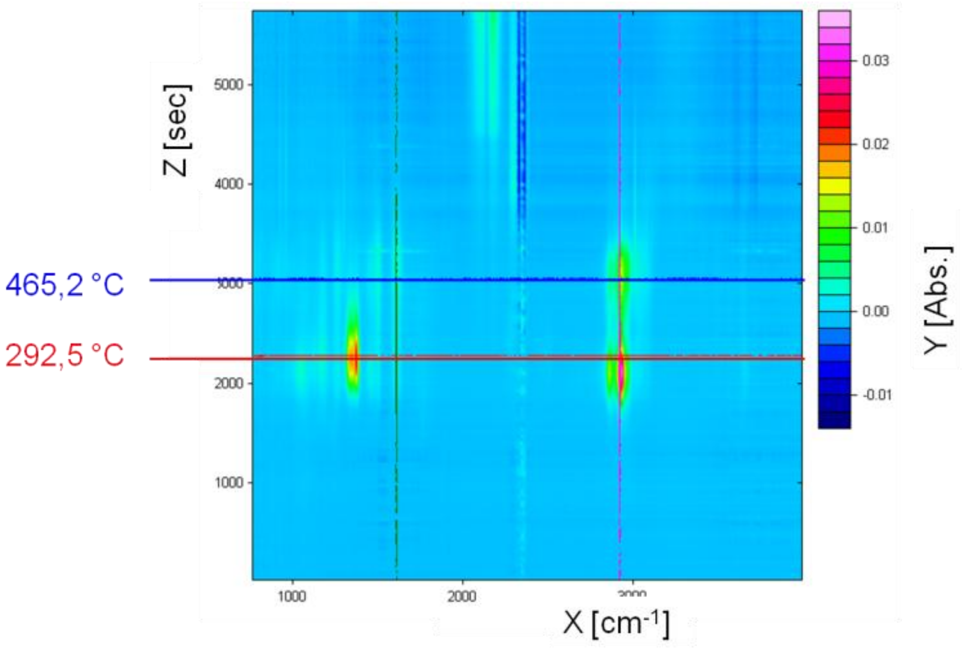


Fig. III: 2D-TGA-FTIR image of amine functionalized (MWCNT-NH$_2$)

2D images (fig. III) of a TGA-FT-IR coupling give a fast overview over the whole measurement. Compared to the 3D-image it dosn´t show the TG-curve but allows to compare time and temperature.

MWCNT-Pellet used for Raman Measurements

Fig IV: Disk (Ø 1,3 cm) of carbon nanotubes after compression molding

The disks prepared for the Raman measurement were prepared by pressing 100 mg of the CNT sample at 5 or 10 t (Ø 1.3 cm) for 5 to 15 min.

The experimental setup for the Raman measurements of powders consists of a holder which is filled with the carbon nanotube powder. The quality of the Raman spectrum might be influenced by the quantity of carbon nanotubes that are placed inside the holder.

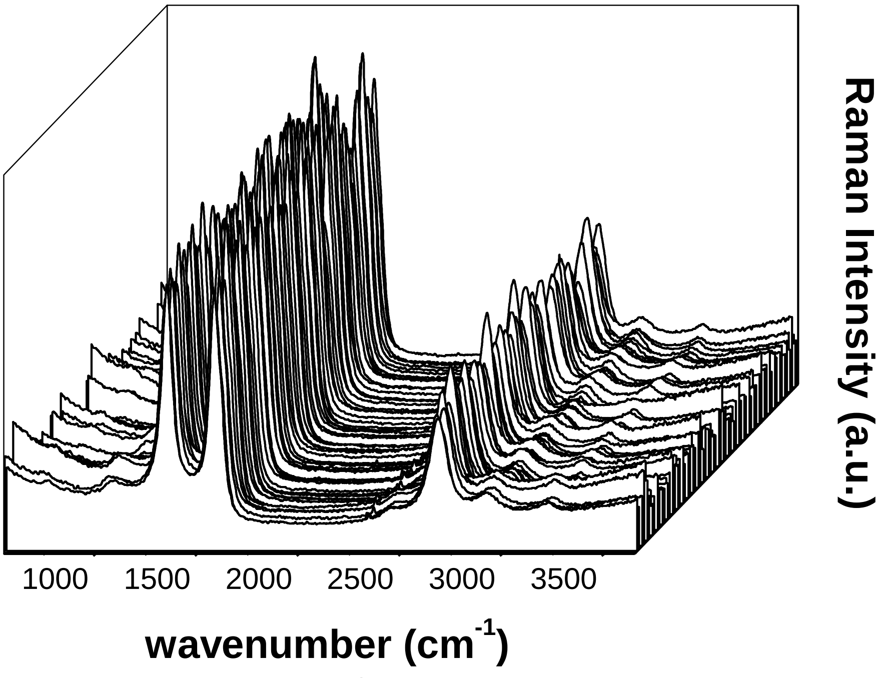


Fig. V: Raman spectra mapping of pristine MWCNT; 300x300 µm, distance between the different measuring points

Fig. V shows the spectra of all 100 different measured points of the mapping experiment. It helps to determine differences between the powder and compression mold samples by giving an excellent overview over all spectra.