

Controlled Functionalization of Carbon Nanotubes by a Solvent-free Multicomponent Approach

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The extensive research carried out on carbon nanotubes (CNTs) along the past years has demonstrated the outstanding mechanical, thermal, electric, and electronic properties of these materials.^{1–5} The number of potential fields of application is increasing, spanning from composite reinforcement to electronics, photovoltaics, chemical/biological/physical sensing, scanning probe microscopy, and other.^{6–10} Most CNT applications require manipulation, interaction, or bonding of the CNTs to other materials, dispersion in solvents, or in high viscosity matrices. These operations are often hindered by the chemical inertness of the CNT surface and by the CNTs highly entangled form. The chemical modification of the CNT surface is an approach generally used to overcome some of these problems.^{11–14}

Covalent functionalization will, in general, lead to the formation of strong and stable interfaces with specific matrices. A widely used functionalization method consists of CNT acid treatment using a combination of nitric and sulfuric acids, leading to extensive oxidation of the CNT surface with formation of hydroxyl and carboxyl groups. The carboxyl groups formed may be further activated with thionyl chloride to react with amines¹³ or engage in carbodiimide-activated esterification reactions.¹⁵ The main disadvantage of the acid oxidation route is that it leads to structural damage and breakage of the CNTs. Thus, for applications that profit from the large CNT aspect ratio, other functionalization routes should be selected. Reactions involving the direct cycloaddition to the π -electrons of the CNTs were successfully performed under mild

ABSTRACT The present work reports the solvent-free, one-pot functionalization of multiwall carbon nanotubes (CNTs) based on the 1,3-dipolar cycloaddition of azomethine ylides using *N*-benzyloxycarbonyl glycine and formaldehyde. The surface morphology of the functionalized CNTs was investigated by scanning tunneling microscopy. The effect of temperature on the reaction was studied by thermogravimetry and X-ray photoelectron spectroscopy (XPS). XPS was a key technique for the detailed chemical analysis of the CNT surface. The formation of two major reaction products was observed, namely a cyclic benzyl carbamate and a pyrrolidine. The concentration of the two products varied with reaction temperature and time. At 180 °C, the main product was the cyclic benzyl carbamate, while at 250 °C the major product was the pyrrolidine. This simple, solvent-free chemical procedure yields CNTs with fine-tuned surface functionality.

KEYWORDS: carbon nanotube · chemical functionalization · X-ray photoelectron spectroscopy · thermogravimetry · scanning tunneling microscopy

conditions leading to little or no CNT breakage. The 1,3-dipolar cycloaddition (DCA) of azomethine ylides is among this class of reactions. It was successfully applied to the functionalization of CNTs in 2002,¹² using a dimethyl formamide solution and heating for five days. The reaction time was reduced to 1 h using microwaves as energy source under solvent-free conditions^{16,17} but was limited to small lab scale production. The effect of microwaves on carbon nanotubes is complex,¹⁸ and it is difficult to ensure temperature control and homogeneous reaction conditions while applying this energy source. With the use of solvent-free conditions and heat, the reaction time could be reduced to 2 h and the process scaled-up to tens of grams of homogeneously functionalized CNTs.^{19,20}

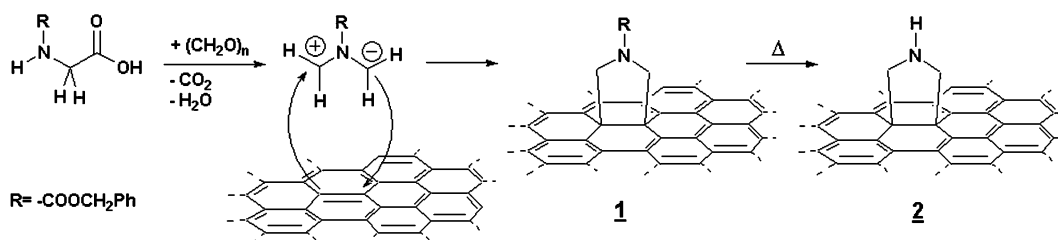
The present study reports the functionalization of CNTs by the DCA reaction using a specific amino acid, *N*-benzyloxycarbonylglycine, that allowed the reaction to proceed under solvent-free, one-pot

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Scheme 1. Functionalization of the CNT surface by the 1,3-dipolar cycloaddition reaction of azomethine ylides.

conditions. Evidence for the formation of two types of functional groups, namely a pyrrolidine and a benzyl carbamate, was obtained. Their relative concentration could be controlled by adjusting the reaction temperature and time. Thus, the CNTs may be prepared with variable surface reactivity, tailored for the application envisaged. Furthermore, this was achieved by a simple multicomponent reaction approach that may easily be scaled-up.

RESULTS AND DISCUSSION

The 1,3-Dipolar Cycloaddition Reaction. The surface modification of multiwall CNTs by the DCA of azomethine ylides is a widely used reaction that yields a pyrrolidine cycloadduct at the CNT surface. The reaction is easy to set up but the common approach requires the use of a large amount of solvent (dimethyl formamide) and long reaction times (5 days).¹² The approach presented in this work was based on the solvent-free reaction of the α -amino acid, *N*-benzyloxycarbonylglycine (Z-Gly-OH) with paraformaldehyde. Heating the solid reaction mixture produces formaldehyde by thermal decomposition of paraformaldehyde; the formaldehyde diffuses through the melted amino acid forming the 1,3 dipolar species represented in Scheme 1. The 1,3 dipoles formed in the CNT vicinity may react with the CNT surface through cycloaddition to originate the benzyl carbamate **1**. Increasing the temperature leads to thermal cleavage of the protecting group of the original amine leading to the formation of the pyrrolidine **2** in Scheme 1, as reported in previous calorimetric and thermogravimetric studies.¹⁹ The product ratio obtained (compounds **1** and **2**) may vary with the reaction conditions.

The pyrrolidine formed at the CNT surface is a nucleophilic group that may react further with other molecules. For example, it may react with different polymers if they contain reactive groups such as carbonate or maleic anhydride, establishing a covalent interaction between the CNTs and the polymer.²⁰

In the present work the CNT surface modification through the solvent-free multicomponent reaction route for the DCA reaction and its dependence on reaction time and temperature were studied. The degree of CNT functionalization was determined by means of X-ray photoelectron spectroscopy (XPS) as the number of nitrogen atoms bonded to the CNT surface relative to

the number of carbon atoms (elemental ratio [N]:[C]). For a given functionalization degree the CNT surface reactivity will depend on the conversion of **1** into **2**. The higher the conversion degree the more reactive will be the CNT surface, and the lower the expected weight loss measured by thermogravimetry (TGA) for a similar yield of N bonded to the CNT surface.

The functionalized CNTs were analyzed by TGA and XPS. TGA measured the weight loss of the CNTs heated from ambient to 800 °C under inert atmosphere, providing the weight of organic functional groups bonded to the CNT surface under the reaction conditions studied. XPS is a technique that analyzes the CNT sample surface within a depth scale of not more than 8 nm. The quantitative determination of the relative number of nitrogen and oxygen atoms bonded to the CNT surface provides evidence for the formation of products **1** and **2** and clarifies the effect of reaction temperature and time on the pyrrolidine yield.

The chemical surface composition of the CNT samples and their thermal stability were analyzed and discussed considering that the main reaction products formed were **1** and **2**, resulting from the cycloaddition reaction. Other side reactions or oxidation products were considered negligible. Thus, the increase in oxygen concentration on the CNT surface after functionalization was associated to the presence of the carbamate **1**.

Carbon Nanotube Surface Analysis. The nanometric scale morphology of the CNTs deposited on highly oriented pyrolytic graphite (HOPG) surfaces was observed by scanning tunneling microscopy (STM). The STM studies were carried out with the Aarhus STM operated under ambient conditions.²¹ The chemical modification along

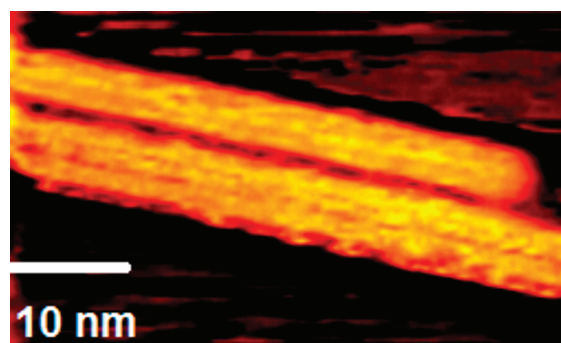


Figure 1. CNTs showing evidence of chemical functionalization of the nanotube wall, obtained by ambient STM. Scanning conditions: $I_t = -1.21$ nA, $V_t = -831$ mV.

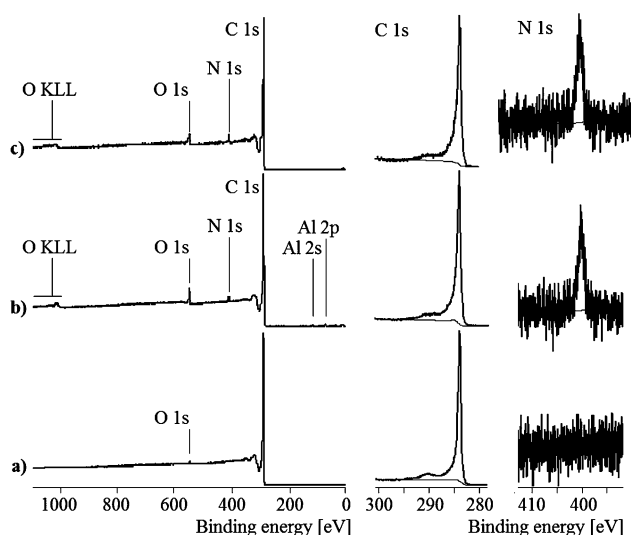


Figure 2. Wide-scan, C 1s and N 1s XPS spectra of an untreated CNT sample (a) and CNT samples after carrying out the DCA reaction at 180 °C for 3 h (b) and at 230 °C for 12 h (c). The abbreviation O KLL designates the oxygen Auger peaks.

the CNTs interrupts the sp² C–C network of the highly electrically conductive graphene layer, forming sp³ C. The smooth, homogeneous surface of the nonfunctionalized CNTs observed under STM turns into an irregular surface with bright protrusions. This observation was discussed previously for the ultrahigh vacuum STM analysis of CNTs functionalized under similar conditions.²² Figure 1 depicts the STM image of CNTs functionalized at 210 °C for 7 h. The image was obtained under ambient conditions and shows the hemispheric end-cap of a CNT extremity, supporting the consideration that the 1,3-dipolar cycloaddition method carried out under the described conditions does not physically damage, or break, the CNT structure. The STM imaging conditions (tunnel current and bias voltage) are detailed in the figure captions.

Figure 2 compares XPS wide-scan spectra of an untreated CNT sample (a) and two CNT samples that were functionalized under different conditions (b and c). The untreated sample showed an intense C 1s peak at a binding energy of ca. 284 eV and a small O 1s peak

at ca. 532.5 eV. After carrying out the DCA reaction at 180 °C for 3 h (Figure 2b) the intensity of the O 1s peak clearly increased, and a considerable amount of nitrogen was detected as a N 1s peak at ca. 400 eV. Aluminum (Al 2p and Al 2s peaks) was present as a contamination from the CNT production process. The binding energy of the Al 2p peak is approximately 74.3 eV, which is in agreement with the binding energy of Al₄C₃. Scanning electron microscopy (SEM) analysis of the CNTs showed the presence of contamination debris dispersed in the CNTs. Energy dispersive X-ray analysis (EDAX) of the debris identified it as aluminum carbide, Al₄C₃. A small amount of silicon dioxide is also observed.

The Al contamination may originate from alumina used in the chemical vapor deposition (CVD) process, which turned into aluminum carbide under the CNT production conditions. The contamination remained after chemical functionalization of the CNTs, as illustrated in Figure 3. SEM images of the Al contamination found in the functionalized CNTs (230 °C) obtained with secondary electrons (a), backscattered electrons (b), and identified by EDAX (c) are presented in Figure 3.

The shape of the high-resolution C 1s spectra of untreated and functionalized CNT samples was characterized by a main component peak and a strong tailing to the higher binding energy side (Figure 4). The conjugation of the π-electrons in the polyaromatic CNT lattice results in a high number of linear combinations forming a quasi-continuum of π and π* orbitals. Electron transitions between these orbitals induce wide shakeup peaks that control mainly the C 1s spectra peak shape and complicate the peak analysis, making it difficult to describe the binding states of carbon. For the deconvolution of the C 1s spectra of the functionalized CNT samples, the C 1s spectrum on an untreated CNT sample was used as a reference (Figure 4). Deviations from the reference spectrum were interpreted as new binding states of carbon, which were formed during the DCA reaction.

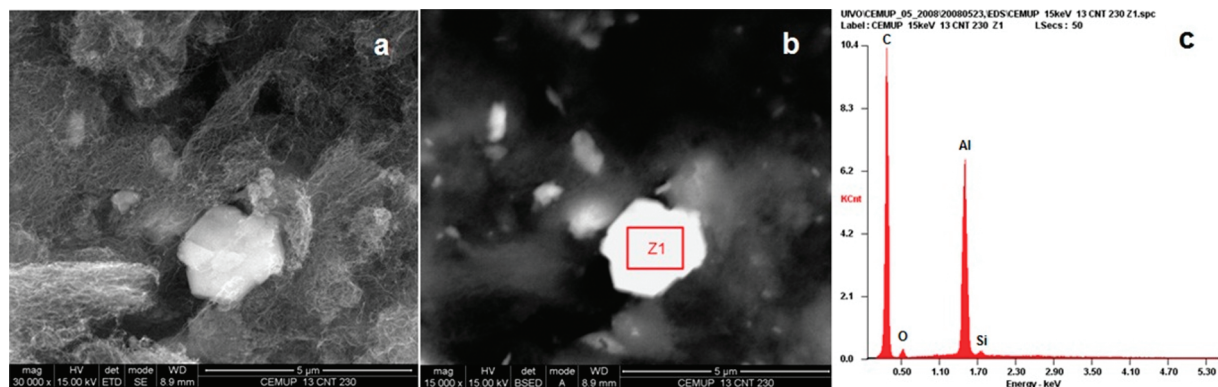


Figure 3. SEM images of CNTs functionalized at 230 °C obtained with secondary electrons (a) and backscattered electrons (b). The area Z1 was analyzed by EDAX (c).

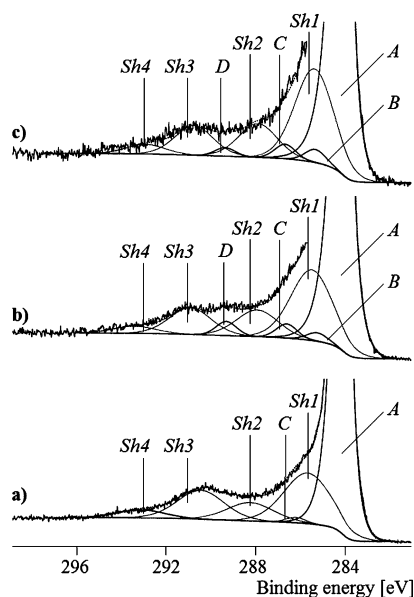


Figure 4. High-resolution C 1s XPS spectra of an untreated CNT sample (a) and CNT samples functionalized at 180 °C for 3 h (b) and at 230 °C for 12 h (c). The intensities of all spectra were normalized using component peak A as reference. To visualize the component and shakeup peaks, component peaks A are shown as cut-out. The abbreviations are explained in the text.

The C 1s spectrum of an untreated CNT sample was deconvoluted into a distinctly asymmetric component peak A showing the sp² carbon atoms of the graphite-like CNT lattice. The asymmetric shape arises from the excited vibration states of the carbon atoms. Four shakeup peaks were necessary to obtain an adequate least-squares fit. A small, not significant, component peak C, may be associated to C–O bonds on the CNT surface. Its binding energy compares with the typical binding energy for phenol OH groups.²³ After carrying out the DCA reaction at 180 °C for 3 h the C 1s spectra was slightly modified, increasing the tailing region at a binding energy of about 287 and 289.5 eV (Figure 4b).

TABLE 1. N and O Elemental Ratios Obtained by XPS, and Weight Loss Results Measured by TGA and Estimated from the XPS Data

reaction temperature (°C)	Reaction time (h)	N:C	(O:C) _{org}	wt _{TGA} (%)	wt _{XPS} estimated (%)
Nonfunctionalized MWNT					
180	1	0.021	0.028	19.5 ± 2	24.1
	3	0.016	0.030	20.4 ± 2	23.5
	6	0.018	0.034	18.5 ± 1	26.2
210	2	0.020	0.039	25.8 ± 2	29.5
	7	0.028	0.020	22.0 ± 2	22.2
230	14	0.020	0.009	20.7 ± 2	13.7
	3	0.036	0.020	11.1 ± 1	24.9
	9	0.028	0.013	13.7 ± 4	18.5
250	12	0.028	0.019	13.4 ± 2	21.7
	3	0.020	0.014	17 ± 2	16.4
	5	0.019	0.002	14 ± 2	9.6
	7	0.022	0.002	13 ± 2	10.6

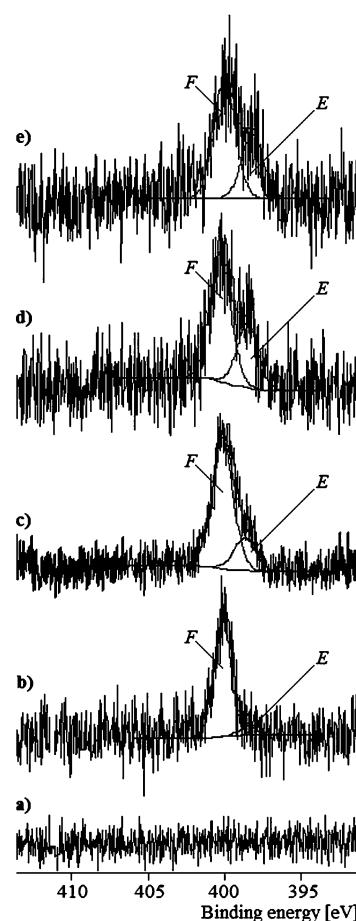


Figure 5. High-resolution N 1s XPS spectra of an untreated CNT sample (a) and CNT samples functionalized at 180 °C for 3 h (b), 230 °C for 3 h (c), 230 °C for 9 h (d), and 230 °C for 12 h (e).

The reaction coupled a considerable amount of oxygen- and nitrogen-containing groups onto the CNT surface (Table 1 summarizes the atomic ratios of the surface-coupled nitrogen [N]:[C] and oxygen [O]:[C]). The functionalities added to the CNT surface caused three additional component peaks (Figure 4b). Component peak B may be associated to amine-like C–N bonds, the carbon atoms of the Ph–CH₂–O groups contribute to component peak C, and the carbonyl carbon atoms of the *N*-benzyloxycarbonyl substituent of the pyrrolidine group were detected as component peak D. The area of component peak B exactly agreed with half of the [N]:[C] ratio determined from the corresponding wide-scan spectrum, indicating that the nitrogen atoms bond to two equivalent carbon atoms bonded to the graphite lattice. The two component peaks C and D showed the presence of the benzyl carbamate **1** (Scheme 1). The areas of the two component peaks C and D were equal and nearly half of the area of component peak B, which is consistent with the stoichiometry of product **1**. The intensities and peak positions of the shakeup peaks were not significantly affected.

The C 1s spectrum of a CNT sample functionalized at 230 °C for 12 h is quite similar to the C 1s spectrum

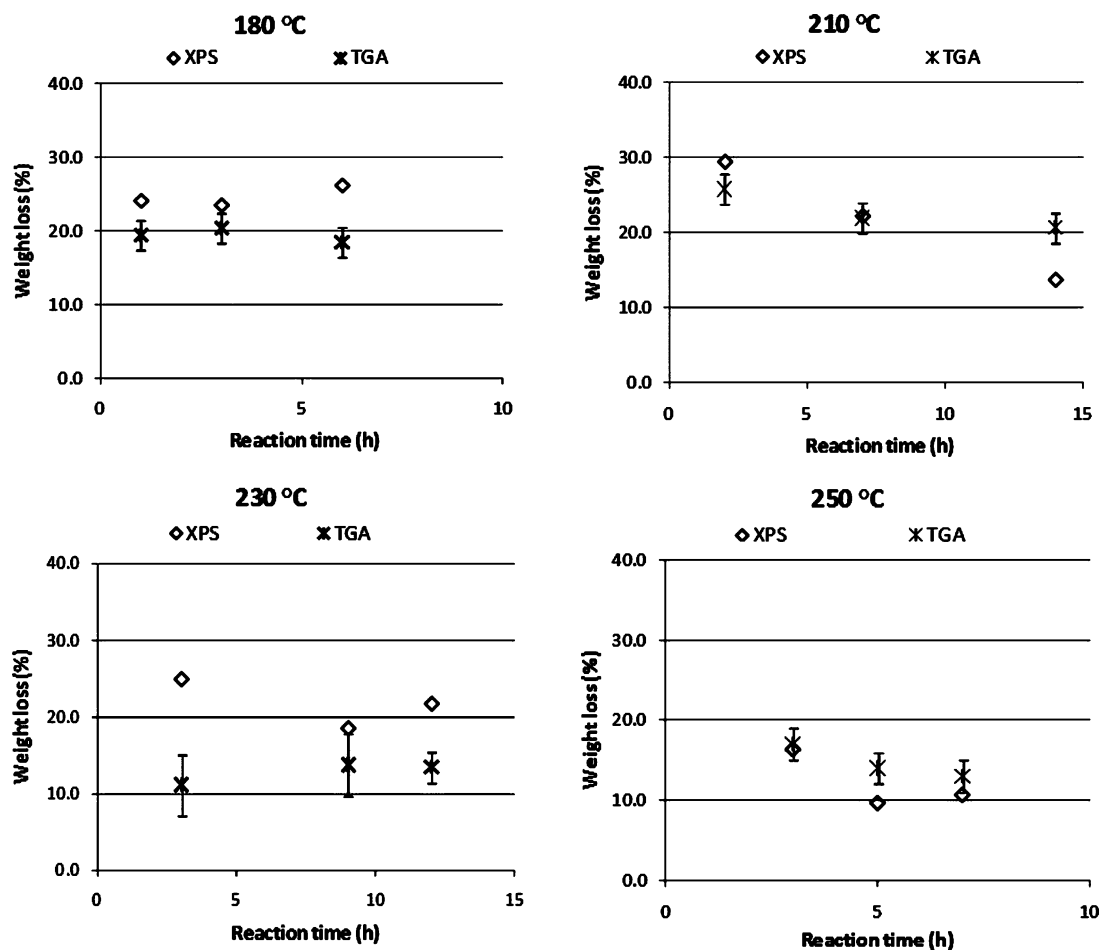


Figure 6. Graphic representation of the weight loss variation with reaction time and temperature, measured by TGA and estimated from XPS results.

of the sample prepared at 180 °C for 3 h (Figure 4c). However, the number of oxygen-containing functional groups added to the CNT surface decreased (Table 1). While the area of component peak B is slightly increased (consistent with the increase of the [N]:[C] ratio), component peak D, arising from the N-substituted pyrrolidine groups, is smaller (Figure 4c). Obviously, the increased temperature and the longer reaction time support the thermal decomposition of species **1**, which is converted into its secondary amine form **2** (Scheme 1).

Normally, the interpretation of the N 1s spectra concerning the binding states of nitrogen is difficult, when it is involved in amino, carbonic acid amide, and carbamate groups. Figure 5 shows a series of N 1s spectra recorded from CNT functionalized at 180 and 230 °C. It can be clearly seen that all N 1s spectra are composed of two component peaks, E and F.

The binding energy of component peaks F was about 400.8 eV, which is typical for nitrogen atoms in carbamate bonds.²⁴ The component peaks E, having a lower binding energy of about 399.1 eV, may be assigned to amino groups.²³ The N 1s spectra confirm the success of the 1,3-dipolar cycloaddition reaction carried out on the CNT and provide quantitative informa-

tion about the relative proportion of the reaction products **1** (area of component peak F) and **2** (area of component peak E).

As mentioned above, an increase in the reaction temperature leads to the formation of secondary amino groups, which are desirable for subsequent surface modification reactions or the covalent coupling of the CNT to polymer matrices (Paiva, M. C.; F. Simon, F.; Novais, R. M., in preparation). It was also observed that longer reaction times forced the thermal decomposition of the carbamate groups.

Weight Loss Analysis. TGA studies performed under inert atmosphere provided the weight of organic groups bonded to the CNT surface, and the results are presented in Table 1. Table 1 also reports the XPS results for the atomic concentration of N and O formed at the CNT surface under the reaction conditions studied, measured on the wide scan spectra. The oxygen concentration reported was corrected for traces of inorganic oxides and for the oxygen content of the non-functionalized CNTs, corresponding to the oxygen in the functional groups, O_{org} . The XPS data may be analyzed in order to estimate the weight loss, considering that the organic groups attached to the CNT surface are mainly compounds **1** and **2**, where the latter is formed

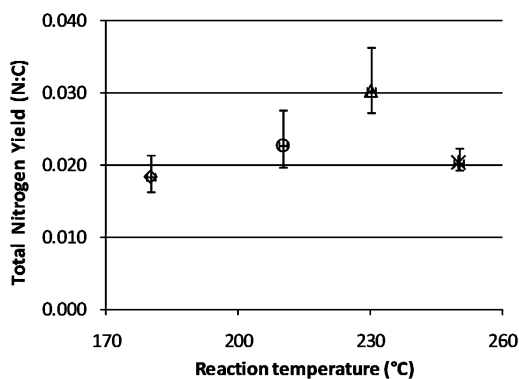


Figure 7. Variation with respect to temperature of the total N bonded to the CNT surface.

by thermal decomposition of the former. Within a reasonable approximation, the weight loss estimated from the XPS results for N and O atom concentration should approach the weight loss measured by TGA under inert atmosphere. Table 1 presents the experimental results obtained for TGA weight loss and the corresponding estimate from the XPS results.

Graphic representation of the weight loss variation with reaction time measured by TGA and estimated from XPS is shown in Figure 6. In general, the XPS estimated and experimental TGA weight loss results are in good agreement. Deviations between the XPS estimates and the measured TGA values may originate from the heterogeneity of the functionalization of the CNTs and the small sample size. Another approximation concerns the CNT oxygen content due to the original oxidation state of the nonfunctionalized CNTs that was considered constant and equal to 0.008, for the O:C el-

emental ratio. The results concur with the assumption that the DCA reaction is the major event under the reaction conditions described.

Influence of the Reaction Conditions on Surface Chemistry.

Previous investigations have shown that the formation of reaction product **1** is an exothermic process.¹⁹ Thus the reaction yield, or the total amount of N that may be bonded to the CNT surface, may vary with the reaction temperature. From a plot of the average total amount of nitrogen bonded to the CNT surface and its variation interval for all the samples functionalized at each reaction temperature, an increase in the overall reaction yield was observed from 180 to 230 °C, and a decrease was observed above that temperature, as illustrated in Figure 7.

The total concentration of N and O bonded to the CNT surface allowed an estimation of the concentration of **1** and **2**, and its evolution with reaction time and temperature. Assuming that the protected amine **1** was the only oxygen containing functional group present, the concentration of group **1** will be equal to the atomic concentration $O_{org}/2$, and the N atoms that are not bonded to oxygen atoms will be in the pyrrolidine form, **2**. The variation of the concentration found for the two functional groups with reaction conditions is represented in Figure 8.

The results demonstrate that in the lower temperature range the main product formed was the benzyl carbamate **1**; as the reaction temperature increased, the concentration of the reactive pyrrolidine **2** increased. At 210 °C the concentration of **2** was dominant only for reaction times greater than 7 h; at 230 °C and above the

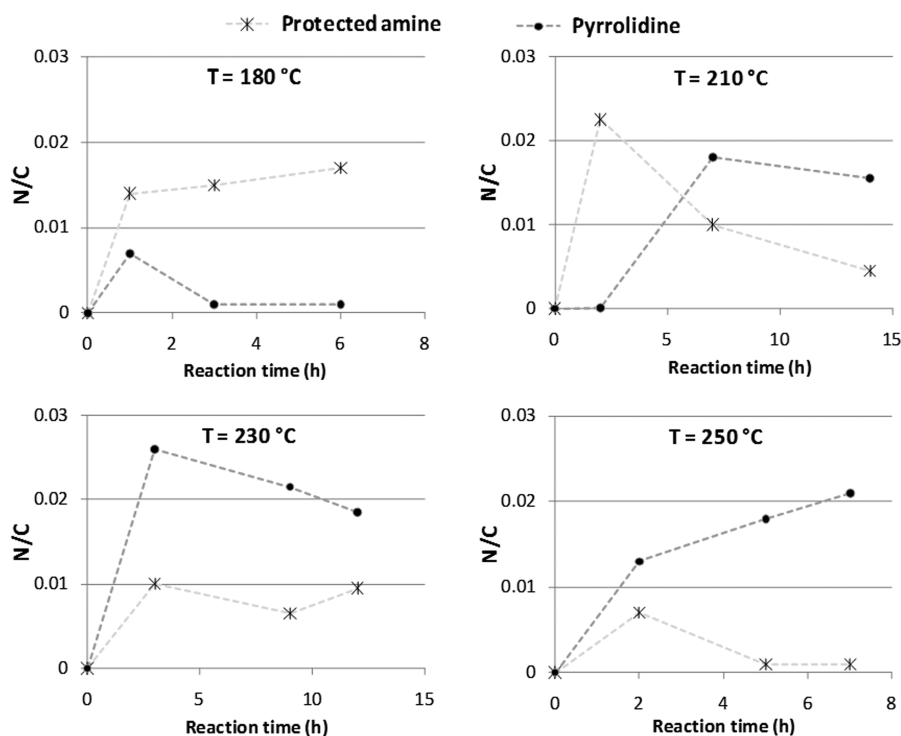


Figure 8. Concentration of the CNT functional groups under different reaction conditions.

concentration of **2** dominated even for shorter reaction times.

The detailed chemical characterization of the modified CNT surface allows the optimization of the functionalization reaction and the tailoring of further reactions or physical interactions with other materials.

CONCLUSIONS

The 1,3-dipolar cycloaddition of an azomethine ylide to CNT was carried out using a multicomponent reaction approach. The DCA reaction was successful even after a short reaction time (1 h) and a relatively low reaction temperature (180 °C) under solvent-free conditions.

EXPERIMENTAL SECTION

Materials and Functionalization Method. The carbon nanotubes used in this study were NC 7000 from Nanocyl. These multiwall carbon nanotubes were produced by catalytic carbon vapor deposition, and present nominal average dimensions of 9.5 nm diameter and up to 1.5 μm length. The chemical functionalization was performed under solvent-free conditions, as described elsewhere.²⁰ The amino acid used was *N*-benzyloxycarbonylglycine (Z-Gly-OH), 99%, from Aldrich, and the paraformaldehyde was reagent grade, from Sigma. An ethanolic solution/suspension of Z-Gly-OH and paraformaldehyde (1:5 molar ratio) was prepared. A suspension of the CNT in the ethanolic solution was gently heated until the solvent was completely removed, so that a thin layer of Z-Gly-OH and paraformaldehyde was deposited on the CNT surface. The solid mixture was heated at different temperatures and times in a round-bottom flask. The reaction temperatures were selected on the basis of previous calorimetric studies reported elsewhere.¹⁹ For studies presented here the reactions were carried out at 180, 210, 230, and 250 °C. The resulting nanotubes were washed several times with ethanol, filtered, and dried.

Carbon Nanotube Analysis. Thermogravimetric analysis was performed on a modulated TGA Q500 from TA Instruments. The samples were heated at 10 °C/min under a constant flow of N_2 , from room temperature to 800 °C. At least five samples were tested for each functionalization condition.

Scanning tunneling microscopy (STM) experiments were performed with a home-built ambient Aarhus STM. The STM images were acquired in the constant current mode. Typical tunneling parameters were 1000–2000 mV and 0.8–1.2 nA for the bias voltage and the tunneling current, respectively, when imaging at the nanometer scale. The samples were prepared by deposition of a few μL of a concentrated solution (or suspension) of the CNTs on a highly oriented pyrolytic graphite (HOPG) surface with fast solvent evaporation. The functionalized CNT solutions were prepared with ethanol in the ultrasonic bath during 1–4 h.

All XPS studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, England). The spectrometer was equipped with a monochromatic Al $K\alpha$ ($h\nu = 1486.6$ eV) X-ray source of 300 W at 15 kV. The kinetic energy of photoelectrons was determined with a hemispherical analyzer set to pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra, respectively.

The samples were prepared as loose powder packed beds on an insulating double-sided adhesive tape. To avoid electrostatic charging during measurements all samples were irradiated by a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same value that was necessary to set the component peak of the graphitic carbon species of the C 1s spectrum to 283.99 eV. This reference value was obtained from analyzing the C 1s spectrum of a mixture made from carbon nanotubes and poly(lactic

The CNT-functionalization reaction was studied in detail by STM, TGA, and XPS techniques. The reaction yield in terms of CNT nitrogen content was estimated by XPS and increased with reaction temperature up to 230 °C. A decrease was evident above this temperature. For each temperature, the concentration of nitrogen bonded to the CNT reached a steady state during approximately the first two hours of the reaction.

The major functionalization product obtained with a reaction temperature of 180 °C was the benzyl carbamate **1**, while at 230 and 250 °C the pyrrolidine **2** was predominant. At 210 °C, the reaction time determined the **1** to **2** product ratio.

acid) (Paiva, M. C.; F. Simon, F.; Novais, R. M., in preparation). One sample was analyzed for each functionalization condition.

Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley.²⁵ The high-resolved spectra were dissected by means of the spectra deconvolution software. Free parameters of the component peaks were binding energy (BE), height, full width at half-maximum, and the Gaussian–Lorentzian ratio.

Scanning electron microscopy was performed using a FEI Quanta 400 FEG ESEM equipped with EDAX Genesis X4M.

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Supporting Information Available: STM images of nonfunctionalized and functionalized CNTs obtained in ambient and UHV conditions; XPS results for the aluminum content of all CNT samples before and after chemical functionalization; FTIR spectra of the nonfunctionalized and functionalized CNTs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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