Dynamic surface rearrangement and thermal stability of nitrogen functional groups on carbon nanotubes

Rosa Arrigo, Michael Hävecker, Robert Schlögl and Dang Sheng Su*

Received (in Cambridge, UK) 24th July 2008, Accepted 28th August 2008
First published as an Advance Article on the web 11th September 2008
DOI: 10.1039/b812769g

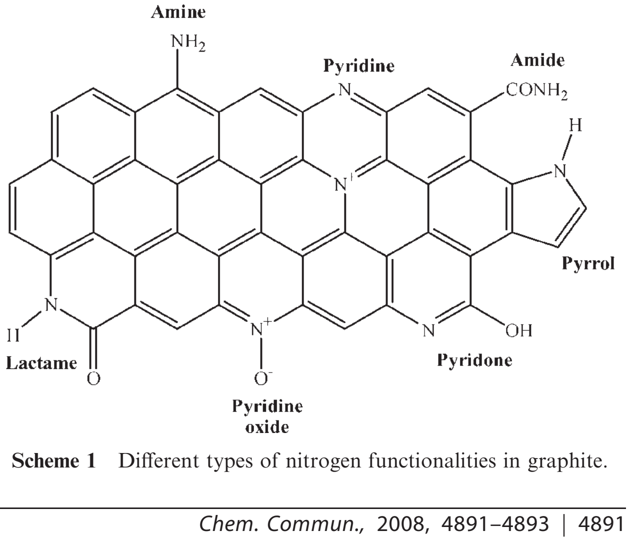
Dynamic surface rearrangement and thermal stability of N-functional groups on carbon nanotubes (CNTs), obtained by functionalization of pristine CNTs with NH_3, were studied by temperature-programmed XPS and MS: a link between the stability of the functional group and decomposition temperature have been established and a conversion into graphitic nitrogen was observed.

Tailoring the electronic, mechanical and chemical properties of CNTs by doping with elements such as N, B and P represents a significant challenge in modern nanotube science. Recently, nitrogen functionalization of CNTs has drawn special interest in heterogeneous catalysis because it induces surface modifications, which can enhance the activity in many catalytic applications in analogy to nitrogen in activated carbon.[1] In fact, N-containing CNTs manifest basic properties that have been exploited in fine chemistry synthesis. Nitrogen functionalization is beneficial for an uniform assembly of metal nanoparticles on CNT surface.[2] These interesting aspects stimulate research aimed at synthesizing N-containing CNTs with a high nitrogen content.[3,4] Different nitrogen functionalities on carbon with quite different properties are reported[5,6] and illustrated here in the Scheme 1.

While the kind of nitrogen functionalities in carbon materials was reported to depend upon the preparation conditions,[7] the thermal stability of the nitrogen functional groups on carbon is still under investigation. This is of importance in view of fact that the applications of the N-functionalized CNTs, for instance in catalysis, may occur at elevated temperature. In this work we study the dynamic surface behaviour of N-functionalized CNTs and the thermal stability of the N-functional groups by temperature programmed X-ray photoelectron spectroscopy (TP-XPS) with on-line mass spectrometry (MS). XPS is a suitable analytical technique for the assessment of nitrogen functionalities in carbon materials. When the sample is subjected to a thermal treatment, any surface modification of the functional groups that occurs can be monitored by XPS and the gas release can be studied by on-line MS. Once all possible functional groups are known, a consistent fit of the recorded spectra during TP-XPS can be done to follow the dynamic behaviour of individual N-functional groups and therefore their thermal stability. Thus, the experiment allows direct characterization of the nitrogen functional groups on the surface and the secondary species generated by their decomposition.

We use a post synthesis treatment, with NH_3, to introduce nitrogen functionalities on the surface of CNTs. In a typical experiment, commercial multiwalled CNTs (MWNT, Pyrograp Products Inc.) are treated with nitric acid (20 g of CNT per litre of HNO_3) at 373 K for 2 h under continuous stirring then rinsed until the washing water turns to a neutral pH. The sample was then dried at 343 K overnight. The aminated sample is obtained by thermal treatment of pre-oxidized CNTs (10 g for each batch) in ammonia flow (0.2 L min^{-1}) at 873 K for 4 h. The surface N abundance determined by XPS using the homogeneous distribution model is 9 at%. The sample is referred as *N*-CNT*873K*.

The XPS N1s core level spectrum of the sample and its deconvolution is reported in Fig. 1. N1s spectra were calibrated *versus* the C1s peak which is generally set to be at 284.6 eV.[8] Three binding energy (BE) regions can be assigned to different nitrogen bonding in the N1s spectrum of model carbonaceous materials:[9] the pyridinic nitrogen region (labelled as N1, at about 398.5 eV), refers to the nitrogen atom contributing to the π system with one *p*-electron; the pyrrol region (labelled as N2, at about 400.1 eV), refers to the nitrogen atom contributing two *p*-electrons to the π system. N2 is composed of the contribution of pyridone, lactam and pyrrol functional groups; the pyridone functionality is the tautomeric form of the lactame functionality. The third region (labelled as N3, at 401–403 eV) refers to the quaternary nitrogen, including protonated pyridine or the "graphitic" nitrogen, where the nitrogen atom is incorporated into the



Scheme 1 Different types of nitrogen functionalities in graphite.

Fritz-Haber-Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany. E-mail: dangsheng@fhi-berlin.mpg.de; Fax: +49 30 8413 4401; Tel: +49 30 8413 5406

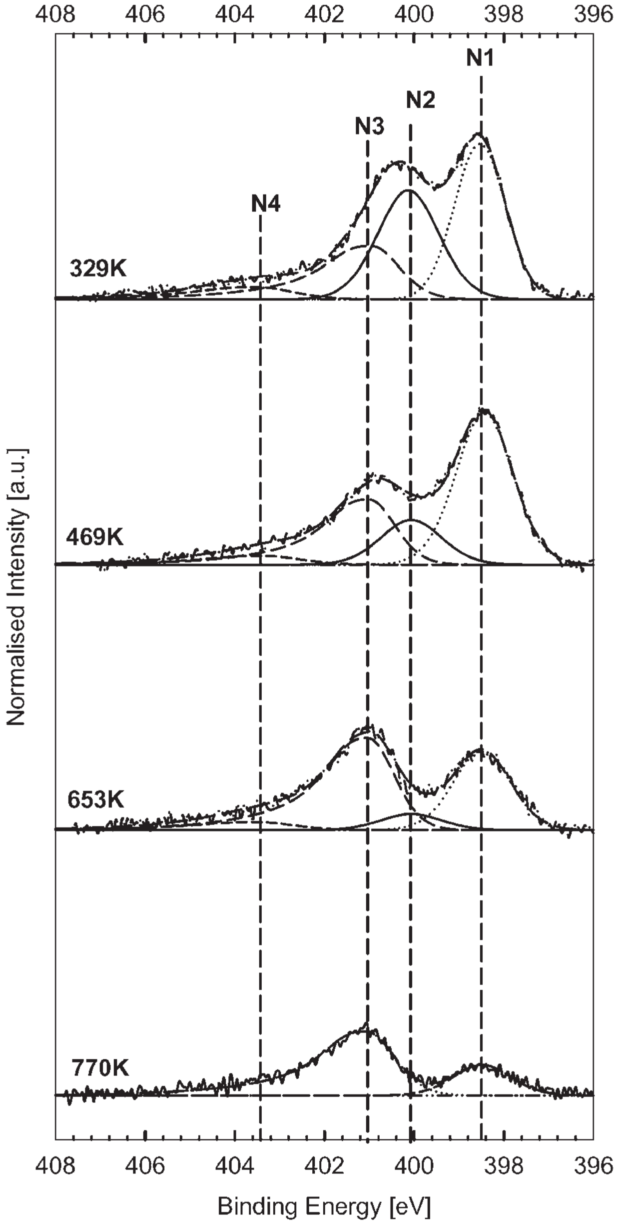


Fig. 1 Deconvoluted N1s core level spectra for sample *N*-CNT*873K* during *in situ* heating. N1 at 398.5 ± 0.1 eV; N2 at 400 ± 0.1 eV; N3 at 401.1 ± 0.1 eV; N4 at 403.4 ± 0.1 eV.

graphene layer and replaces a carbon atom.[13] Furthermore, a peak labelled as N4 with a binding energy shift of +5 eV compared to pyridine is assigned to pyridine oxide. No contribution of amine or amide between 399–400 eV has been found.[10] Table 1 summarizes the literature data concerning assignment of the binding energies related to nitrogen species in carbon materials, and the binding energy values used in the present work for fitting the XPS spectra.

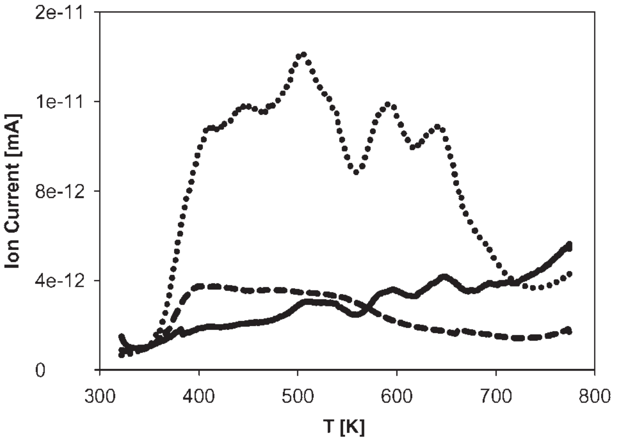


Fig. 2 Mass spectrum during *in situ* TP-XPS for *N*-CNT*873K*: *m*/*z* 27 (dotted line); *m*/*z* 30 (dashed line); *m*/*z* 14 (full line).

Fig. 2 displays the TPD-mass spectra during TP-XPS. As it was reported earlier,[11] nitrogen functional groups in carbon materials decompose during heating into NH_3, HCN, and, in the most oxidized sample, into NO. In this experiment, the main detectable signals are HCN (*m*/*z* 27), NO (*m*/*z* 30) and N_2 (*m*/*z* 14). The *m*/*z* 27 signals (Fig. 2 dotted line) exhibit several features over the temperature range, corresponding to two different functional groups. The oscillation of this signal between 400 K and 660 K indicates a dynamic change of the N-functional groups on carbon rather than a simple decomposition into gaseous molecules. In comparison with HCN, the signal assigned to NO is relatively low, and its evolution characteristics differ too. In particular it is linked to the lower thermal stable nitrogen functionalities. The *m*/*z* 14 is strictly related to the nitrogen functionalities, since it comes from fragmentation of those species. In fact it presents the same oscillation as *m*/*z* 27, especially at high temperatures. It is still unclear whether the mechanism of formation for these species is homogeneous, as a consequence of gas phase reactions between unstable intermediate radicals generated during the cracking of the functional groups, or heterogeneous, if they are generated by surface rearrangements of the functional groups. According to the literature,[12] decomposition of functional groups such as nitrile ions gives rise to HCN when water is present. At low temperatures the ions are attributed to the decomposition of lactame groups, while at higher temperatures they are attributed to pyridine. Understanding the cause of NO formation is more complicated. NO formation is probably due to a dynamic surface rearrangement of moieties containing nitrogen and oxygen, *e.g.* lactame, giving rise to NO in the mass spectrum. It could be also related to the decomposition of a pyridine oxide species formed during the experiment. From Fig. 2, it is clear that some of the nitrogen functionalities initially present in the sample are released in the gas phase, with a consequent decrease in the overall nitrogen

Table 1 N1s core level XPS assignment for carbon material

Type of nitrogen	Pyridine nitrogen	Pyrrol and pyridone (lactame)	Quaternary nitrogen	*N*-oxide of pyridine nitrogen
BE (eV) literature	398.3–398.7[12–18]	400.1–400.5[12,14,16]	401.2–401.4[12,15–18]	402.8–403.8[12–15,18]
This work (eV)	398.5	400.1	401.1	403.5

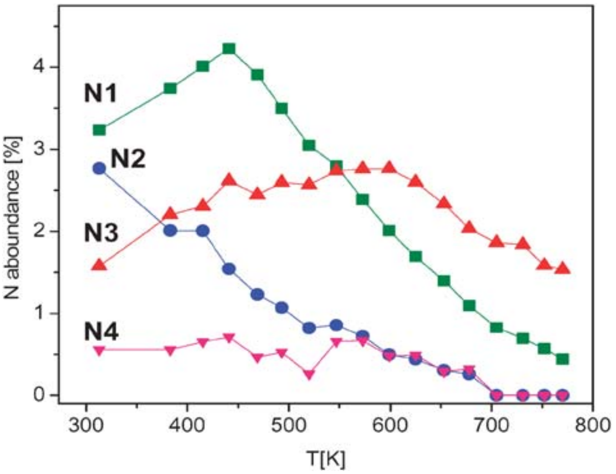
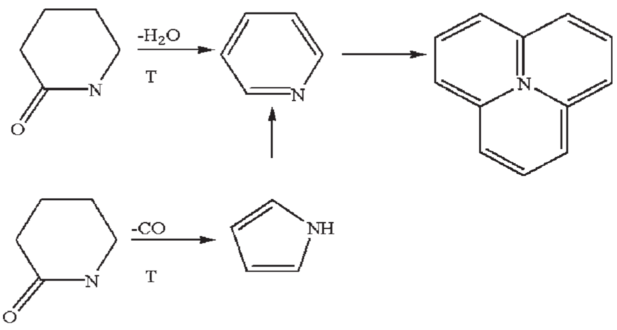


Fig. 3 Evolution of different N-species during TP-XPS for *N*-CNT 873:N1 (green curve); N2 (blue curve); N3 (red curve); N4 (pink curve).

content. However some functional groups are retained and undergo dynamic surface rearrangement during heating. The evaluations of the various components N1–N4 *versus* temperature are plotted in Fig. 3. The N2 functionalities decrease continuously with increasing temperature. Since at the same time the N1 and N3 components in the XPS spectra increase, we can presume that lactame and pyrrol functional groups (N2) convert partly to these species.

Since trace water is detected by MS while the N2 component decreases, we assume that lactam species are present, with a binding energy of 400.3 eV. However, the presence of pyrrol groups cannot be excluded. Lactam can dehydrate to pyridine functionalities, or can be thermally decomposed through the formation of intermediate amide moieties that can further decompose giving both m/z 27 and m/z 30, corresponding to the first main feature in the mass spectrum. The pyridine total abundance reaches a maximum at 450 K and above this temperature starts to decrease (N1 curve in Fig. 3) while N3 still increases, reaching a maximum at an higher temperature (600 K). Even in this case, a competition occurs between the structural transformation of pyridine into N3 and decomposition in the gas phase that give rise, above 600 K, to the second main feature in the m/z 27. Such processes occur in a wide range of temperatures, so that the two pathways are overlapping each other. The N3 species is the most thermally stable species, it is generally referred to in the literature as quaternary nitrogen but the exact nature of this functionality is still poorly established. Earlier, it was reported that an hypothetical structure of this functionality could be as reported in Scheme 2.[13] Thus, the surface reassembles into graphite cluster during heating, leading to aromatization with the introduction of a small amount of N in the graphitic structure. Scheme 2 summarizes the modification of nitrogen functionalities during thermal treatment. Similar results have been reported earlier[13] for NH_3 treatment on activated carbon.



Scheme 2 Nitrogen insertion pathway in CNT.

In summary, N-containing CNTs are prepared by post-synthetic functionalization with NH_3. It has been shown that TP-XPS is a suitable tool for understanding the N1s spectrum and assessing nitrogen functionalities. Furthermore, it is possible to relate the mass signal and binding energy to certain specific functional groups. Although the decomposition of the functional group competes with the conversion to another functional group, through a dynamic surface rearrangement that might depend upon the heating rate and the experimental pressure condition, a general trend was observed: initially functional groups with a binding energy at 400.3 eV partly decompose through formation of HCN, and partly convert into pyridine groups. Above 450 K, the pyridine is transformed into graphitic nitrogen or decomposes, giving rise to further formation of HCN, and above this temperature graphitic nitrogen is the main species. Since the distribution of surface functional groups remaining in the carbon nanotube's surface, depends on the temperature, the procedure we present in this work allows us to tune the acidic and basic properties of carbon nanotubes.

Notes and references

1 B. Stöhr, H. P. Boehm and R. Schlögl, *Carbon*, 1991, **29**, 707.
2 X. Li, Y. Liu, L. Fu, L. Cao, D. Wei, G. Yu and D. Zhu, *Carbon*, 2006, **44**, 3139.
3 R. Sen, B. C. Satishkumar, A. Govindaraj, K. R. Harikumar, G. Raina, J. Zhang, A. K. Cheetham and C. N. R. Rao, *Chem. Phys. Lett.*, 1998, **287**, 671.
4 M. Terrones, R. Kamalakaran, T. Seeger and M. Rühle, *Chem. Commun.*, 2000, **23**, 2335.
5 L. R. Radovic, I. F. Silva, J. I. Ume, J. A. Menéndez, C. A. Leon Y Leon and A. W. Scaroni, *Carbon*, 1997, **35**, 1339.
6 C. P. Ewels and M. Glerup, *J. Nanosc. Nano.*, 2005, **5**, 1345.
7 S. van Dommele, A. Romero-Izquirdo, R. Brydson, K. P. de Jong and J. H. Bitter, *Carbon*, 2008, **46**, 138.
8 N. M. Rodriguez, P. E. Anderson, A. Wootsch, U. Wild, R. Schlögl and Z. Paal, *J. Catal.*, 2001, **197**, 365.
9 J. Casanovas, J. M. Ricart, J. Rubio, F. Illas and J. M. Jiménez-Mateos, *J. Am. Chem. Soc.*, 1996, **118**, 8071.
10 Amide and amine functional groups are formed at lower NH_3 treatment temperature (manuscript in preparation).
11 J. P. Boudou, Ph. Parent, F. Suárez-García, S. Villar-Rodil, A. Martínez-Alonso and J. M. D. Tascón, *Carbon*, 2006, **44** 2452.
12 R. J. J. Jansen and H. van Bekkum, *Carbon*, 2007, **32**, 1507.
13 J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu and K. M. Thomas, *Carbon*, 1995, **33**, 1641.
14 P. H. Matter, L. Zhang and U. S. Ozkan, *J. Catal.*, 2006, **239**, 83.
15 E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, J. Find, U. Wild and R. Schlögl, *Carbon*, 2002, **40**, 597.
16 A. N. Buckley, *Fuel Proces. Technol.*, 1994, **38**, 165.
17 K. Stańczyk, R. Dziembaj, Z. Piwowarska and S. Witkowski, *Carbon*, 1995, **33**, 1383.
18 M. A. Wójtowicz, J. R. Pels and J. A. Moulijn, *Fuel*, 1995, **74** 507.