Nitrogen in highly crystalline carbon nanotubes

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Abstract. Multiwall carbon nanotubes (MWCNTs) with an unprecedented degree of internal order were synthesised by chemical vapour deposition (CVD) adding a nitrogen-containing compound to the hydrocarbon feedstock. Ferrocene was used as the metal catalyst precursor. The remarkable crystallinity of these nanotubes lies both in the isochirality and in the crystallographic register of their walls, as demonstrated by electron diffraction and high resolution electron microscopy experiments. High resolution transmission electron microscopy analysis shows that the walls of the nanotubes consist of truncated stacked cones, instead of perfect cylinders, with a range of apex angles that appears to be related to the nitrogen concentration in the synthesis process. The structure of armchair, zigzag and chiral nanotubes is modelled and discussed in terms of density of topological defects, providing an interesting comparison with our microscopy experiments. A growth mechanism based on the interplay of base- and tip-growth is proposed to account for our experimental observations.

1. Introduction
Nitrogen doping of carbon nanotubes has attracted interest in view of possible modifications of the electronic and mechanical properties of the tubes [1, 2, 3]. Different synthesis conditions, in particular for pyrolysis of carbon- and nitrogen-containing precursors in the presence of an iron catalyst, lead to the encapsulation of molecular nitrogen in the core of multiwall tubes, which is interesting for fundamental studies as well as for gas storage applications [4, 5]. Recently a similar pyrolytic reaction has been reported to have yielded multiwall carbon nanotubes with an unprecedented level of order [6]. From electron diffraction analysis 30% of the tubes were identified as purely zigzag shells, 20% as purely armchair, and 50% as mixed zigzag and armchair orientations. The present work is aimed at the further study of this kind of carbon nanotubes by the use of transmission electron microscopy (TEM).

2. Experimental methods
Carbon nanotubes were grown by chemical vapor deposition (CVD) in a furnace reactor [7], at 760°C under argon, from a solution of 2 wt.% ferrocene in toluene diluted with 0 to 40% 1,4-diazine (C₄H₄N₂). Dense films of nanotubes were grown on silicon substrates, with an overall content of nitrogen ranging from 0 to 3 wt.%, as shown by elemental analysis.

The specimens were removed from the silicon substrates and dispersed onto holey carbon Cu grids for TEM analysis. The high resolution TEM experiments were performed on a Jeol 4000EX (400kV) microscope with C₄₀ of 1.7 mm and point resolution of 0.17 nm. Electron energy
Figure 1. A high resolution image of the walls and the core of a bamboo-like nanotube is shown. FFTs of both regions indicate a highly crystalline ABAB arrangement of the graphitic lattice, with clear zigzag signature, i.e. with the [100] direction parallel to the tube axis.

loss (EELS) experiments were performed on a FEI CM300 (300kV). All specimens appear to be stable under the electron beam during high resolution imaging. No beam damage was observed during TEM analysis.

3. Results and discussion
Nanotubes grown from pure toluene/ferrocene precursors appear to have a well defined morphology, with thick parallel walls and narrow inner core often filled with catalytic iron nanoparticles. The outer diameter of the tubes ranges from 50 to 110 nm, with a strong peak at about 90 nm. The average inner diameter is 13 nm, so the ratio between the two diameters is about 8. As azine is introduced in the synthesis process, two different tube morphologies begin to evolve. The most abundant at low N concentrations is the bamboo-like morphology, with intersects (10-20 layers thick) dividing the tube in regularly spaced compartments. The second type of tubes, referred to as web-like, have less compact and regular compartments across the core. The web-like membranes are usually 2 atomic layers in thickness. The outer diameter of the tubes grown in the presence of nitrogen is about 30-40 nm, with an outer to inner diameter ratio of 3 to 2.

A similar morphology evolution was observed by M. Glerup and coworkers in [8]. However they report of partially amorphous, defective tubes, whereas in the present study the degree of crystallinity in the tube walls is extremely high.

Well crystallized catalytic particles were found at the base of the tubes in all specimens, suggesting a base growth mechanism. Metallic particles of conical shape were also observed at the tip of a large fraction of web-like tubes, hinting at a more delicate interplay of tip and base growth. High resolution TEM analysis reveals that the catalytic particles at the tip of the tubes are single crystal Fe<sub>3</sub>C, usually oriented with the [100] direction parallel to the tube axis. This preferential orientation implies an epitaxial relationship between Fe<sub>3</sub>C(010) and graphite(002) [9]. We need to emphasize that this analysis was performed ex situ, and therefore it does not provide conclusive evidence for the role of the carbide as a catalyst for the growth.
Figure 2. The mismatch is plotted as a function of c/a and the cone apex semiangle for zigzag and armchair tubes. Average c/a and angles (and relative circumferential mismatch) obtained from experimental data are superimposed on the graphs.

An essential feature of the nanotubes grown in the presence of nitrogen is that the walls are no longer formed by concentric cylinders, but by stacked truncated cones, arranged to give a constant outer and inner tube diameter. Although accurate statistics are difficult, for bamboo-like tubes the apex semiangle, $\phi$, is seen to vary between 2° and 7° at 1 N wt.%, and between 3° and 9° at 3 N wt.%. In the case of web-like tubes, $0^\circ < \phi < 4^\circ$ and $1^\circ < \phi < 7^\circ$ were observed for 1 and 3 N wt.%, respectively. In average this trend seems to indicate an increased ability to form shallower cones when the nitrogen doping is higher.

From chemical maps acquired using the nitrogen edge to form the EFTEM image, it is evident that nitrogen is mainly present in the core of the web-like tubes where it appears to fill the space isotropically. The nitrogen content is not the same in all web-like tubes and it is very low if not absent for bamboo-like tubes. In the literature many reports can be found stating the extreme reactivity of N doped CNTs to the small electron probes used in scanning TEM (STEM) mode [5]. In the present study the same severe beam damage was observed, and therefore electron energy loss (EEL) spectra were acquired in TEM mode, with an electron probe of the same diameter as the tube. This was found to reduce beam damage to a negligible level, allowing longer acquisition times and better signal integration. Amorphous carbon contamination was also avoided. From the position and the shape of the nitrogen edge we infer the presence of molecular nitrogen in most of our web-like tubes [4].

Electron diffraction, high resolution imaging and x-ray diffraction data confirm that the nanotubes grown in the presence of nitrogen crystallize with long range ABAB periodicity. Figure 1 shows a portion of a bamboo-like structure, with Fast Fourier Transform (FFT) analysis of the walls and the core indicating the zigzag character of the nanotube. From geometrical considerations it is easy to see that a crystal of identical stacked cones can be generated with
ABAB periodicity, and the circumferential mismatch in the lattice can be written in terms of the cone apex semiangle $\phi$ and of the ratio $c/a$: $\Delta a = m_i a - \pi c / \cos \phi$, where $m_i$ is an integer number. In particular for the zigzag case we have $\Delta a = a - \pi (c/a)(1/cos \phi)$, and for the armchair case $\Delta a = \sqrt{3} a - (\pi / \sqrt{3})(c/a)(1/cos \phi)$). Figure 2 shows the variation of the circumferential mismatch with $c/a$ and cone apex semiangle, calculated for zigzag and armchair configurations. The mean $c/a$ ratio and $\phi$ determined from experimental data is superimposed (with error bands), showing that in the zigzag tubes both the ratio $c/a$ and its standard deviation are larger than for the armchair tubes, whereas the range of measured $\phi$ is smaller. This trend is reflected by the mean value of $\Delta a$ calculated from experimental data and its standard deviation. The calculations show good agreement with the experiment.

A qualitative explanation for the smaller circumferential mismatch associated with the zigzag orientation comes from our model for the graphitic cones. Except in the limited number of cases for which the rolled up hexagonal lattice gives exact overlap of the atoms at the seam, in general the seam region will include some defects, namely pairs of 5- and 7-membered rings. A 5-7 pair always imposes a distortion of the graphitic lattice, so that the hexagons surrounding the defect tend to assume a zigzag orientation along the cone axis. Therefore, in the near-zigzag cones the unit $a$ is very close to the lattice vector all around the circumference, whereas for most near-armchair cones the vector $a$ varies from $\sqrt{3}a$ to $a$ around the circumference. This has an obvious impact on the circumferential mismatch as well as the overall strain on the lattice.

As for the origin of the topological defects in the cones, it is known that nitrogen in its pyrrole bonding configuration can induce pentagonal defects into a graphitic lattice [10, 11]. The N1s binding energy for nitrogen bonded to 3 carbon atoms in a pyrrole-like structure is 400.1 to 400.7 eV[12], compatible with our EELS data. Although the strongest signal in our spectra certainly comes from gas phase $N_2$ trapped inside the core of the nanotubes, we also have evidence for nitrogen bonded to carbon atoms within the graphitic lattice (but this is a noisier, weaker signal, suggesting a lower concentration of $N$ within the lattice).

4. Conclusions
Pyrolysis of toluene/azine mixtures in the presence of ferrocene at 760°C appear to favour the formation of highly crystalline carbon nanotubes. The ABAB stacking of the graphitic shells was confirmed by high resolution TEM. A model for the conical tube shells based on the presence of 5-7 topological defects was proposed and compared with our experimental data.

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