Novel nanoscale gas containers: encapsulation of N_2 in CN_x nanotubes

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Gaseous N_2 has been efficiently introduced in the hollow cavities of aligned CN_x nanotubes (15–80 nm od) by pyrolysing a jet (spray) solution of $Fe(C_5H_5)_2$ and $PhCH_2NH_2$ in an Ar atmosphere at 850 °C; the aligned material consist of large arrays (2.5 cm^2) of CN_x ($x < 0.05$) 'bamboo-like' nanotubes (< 100 μm in length); high resolution electron energy loss spectroscopy (HREELS) line-scans and elemental mapping studies reveal that N gas was encapsulated within the hollow compartments of the CN_x nanotubes; these results demonstrate for the first time, that CN_x nanotubes can be used to fabricate gas storage components.

Carbon nanotubes[1] can behave as efficient gas and metal containers. In particular, it has been demonstrated that metals, metal carbides, oxides, chlorides, *etc.*[2–4] can be introduced into the carbon nanotube cores by methods involving: (a) chemical treatments[5] (by boiling suspensions of nanotubes in aqueous nitric acid for several hours), (b) arc discharge[6] (by arcing graphite electrodes packed with a metal); (c) solid state reactions[7] (by heating nanotubes with halides under vacuum) and (d) electrochemical techniques[8] (by passing a current through graphite electrodes in molten ionic salts at *ca.* 600–700 °C). Unfortunately, these are not able to encapsulate gaseous substances.

Recent studies have revealed that H_2 and Ar can be stored in single[9,10] and multiwalled carbon nanotubes,[11] respectively. However, these processes involve at least two steps including the material production and the gas introduction. In the case of multiwalled nanotubes (MWNTs), Ar has been introduced using high Ar pressures for 48 h at 650 °C. Here we report an alternative route to introduce N_2 inside multiwalled CN_x ($x < 0.05$) 'bamboo-like' nanotubes using a single step reaction process [spray pyrolysis of $Fe(C_5H_5)_2$ (ferrocene) and $PhCH_2NH_2$ (benzylamine) solutions]. The products were studied using scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and HREELS.

The pyrolysis apparatus[12] consists of a 300 mm long furnace fitted with a quartz tube (id 10 mm, 800 mm long). One end of the tube is attached to a Pyrex cone (id 0.35 mm), which is connected to a container used for storing and releasing ferrocene/benzylamine solutions. A nozzle (consisting of a capillary) is contained in the Pyrex cone with an exit diameter of 0.5 mm. The reaction tube was preheated to 850 °C; subsequently the solution (0.2 g. ferrocene in 2 ml benzylamine) was released and sprayed by flowing Ar (Messer Griessheim 99.999%) around the cone/nozzle area into the hot zone. The spraying time lasted between 5 and 10 min, usually using 1 ml of the solution. The furnace was maintained at this temperature for an additional 15 min in order to anneal the products.

SEM studies were carried out using a JEOL-JSM 6300F operated at 2–5 kV and a Zeiss DSM 982 Gemini operated at 1–2 kV. HRTEM observations were made using a JEOL-JEM4000 EX operating at 400 kV. Energy-dispersive X-ray (EDX) spectroscopy data were obtained using a Noran Ins. detector fitted within the JSM 6300F microscope. HREELS studies were performed in a dedicated STEM VG-HB 501UX equipped with a Gatan Digi-PEELS 766 detector.

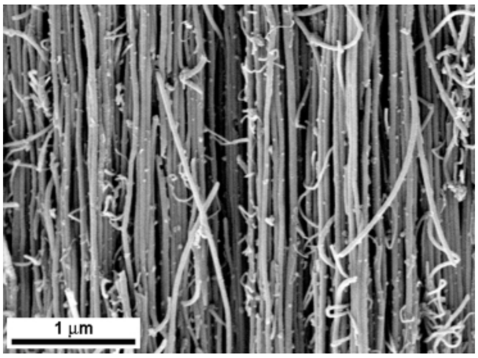

Fig. 1 SEM image of a typical film of aligned CN_x nanotubes of uniform diameter (*ca.* 40 nm od).

The pyrolysed material, scratched from the internal tube surface (hot zone), consists of large black and shiny films of area 2.5 cm^2 and 100–200 μm thick. SEM studies reveal that the films are composed of aligned tubular structures (100 μm long, 15–80 nm od). Fig. 1 shows a typical region of aligned nanotubes observed within the films.

TEM and HRTEM studies indicate that the material mainly consists of nanotubes exhibiting compartmentalized morpholo-

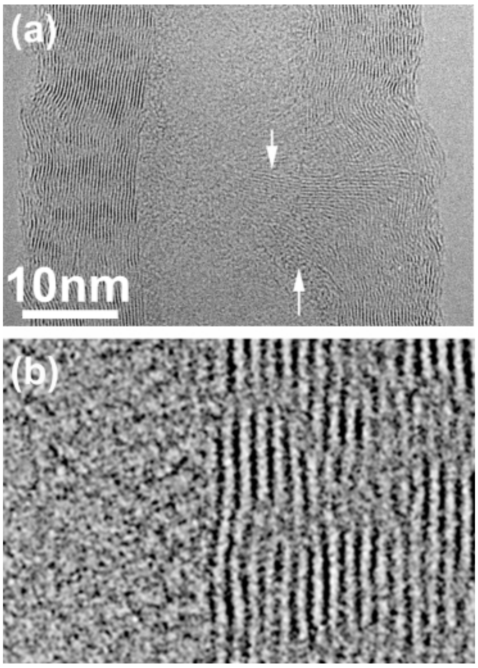

Fig. 2 HRTEM images of a CN_x nanotube: (a) tube segment showing 'graphitic' walls parallel to the tube axis as well as an inner core. It is important to note that the inner core contrast (amorphous-like) suggests the presence of a foreign non-crystalline material. In addition, some inter-linked planes appear to cross the core of the tube, creating compartments (arrows); (b) higher magnification of a CN_x nanotube exhibiting the degree of crystallinity of walls as well as the amorphous-like core (interlayer spacing 0.34 nm).

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gies resembling ‘bamboo-like’ structures, similar to those observed in CN_x nanofibres.[13,14] Fe particles (identified by EDX and electron diffraction) were also observed at the tips of the nanotubes. This confirms that catalytic nanotube growth took place. It is noteworthy that the presence of other carbonaceous material within the samples was notably absent. HRTEM images showed that the tubes were hollow with wide inner cores (> 10–20 nm), but compartmentalized forming pockets caused by inter-linkage of graphitic planes across the inner core of the tubes [Fig. 2(a)]. Close inspection of the tubular structures confirmed that the walls consisted of parallel graphite-like sheets [< 30 walls; Fig. 2(b)]. We also note that the hollow core of the tubes exhibited an amorphous-like appearance [Fig. 2(a)], suggesting that a foreign material was encapsulated.

EEL spectra of the nanofibres revealed the presence of ionisation edges at *ca.* 284.5 and 400 eV corresponding to the C and N K-excitations. The near edge fine structure of the carbon K-edge confirms that the material is ‘graphitic’. Interestingly, a first EELS measurement on a typical CN_x tube revealed a high intensity peak at (401 ± 0.5) eV, clearly indicating the presence of molecular N_2[15] [Fig. 3(a)]. Following this measurement a ‘hole’ was formed due to the heavy electron irradiation. A subsequent spectrum recorded in the same area revealed a completely different N-K edge exhibiting a π^*-peak at (399 ± 0.5) eV and a broad σ^*-peak [Fig. 3(a)], which is commensurate with the incorporation of N within the sp^2-carbon network (usually observed in CN_x nanofibres[13,14]). The latter observations suggest that N gas was trapped within the hollow nanotube core, and after our first measurement the effect of focusing the electron beam on the tube caused the tube to open, thus releasing the encapsulated N_2 gas. Once a ‘hole’ was created, N_2 gas was not detected in neighboring areas.

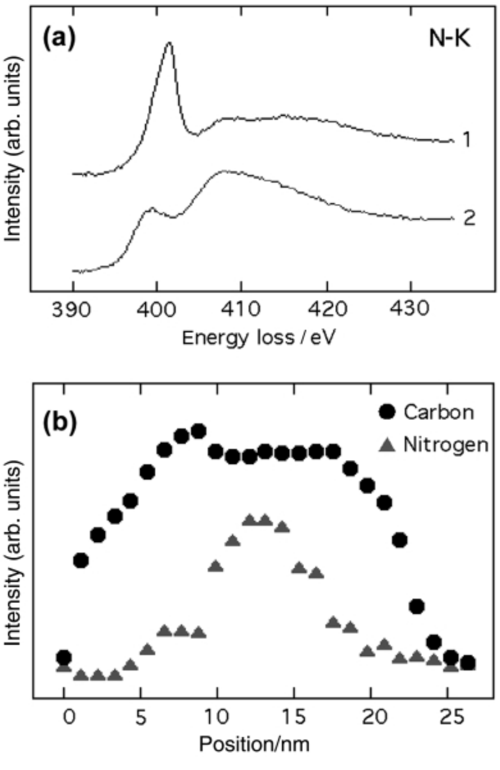

Fig. 3 (a) EEL spectra of the N-K edge representative of a CN_x nanotube. The first measurement (spectrum 1) reveals the presence of molecular nitrogen (peak at 401 ± 0.5 eV). In a second measurement (spectrum 2) recorded at the same position, the sharp peak disappears and a maximum appeared at 399 ± 0.5 eV, corresponding to N incorporated within a C-network. During measurements, we noted that a ‘hole’ (caused by electron irradiation) was only created when molecular N was trapped inside the tube; (b) concentration profiles of C and N across the diameter of a 25 nm CN_x nanotube derived from EELS line-scans. These indicate the presence of C on the periphery and N mainly within the inner core of the structures. The central ‘dip’ in the carbon profile is commensurate with an internal core, filled with N.

In order to confirm the presence of N in the nanotube core, HREELS line scans were performed across several tubes. A typical line-scan across the tube axis [Fig. 3(b)] reveals that the C and N concentration profiles ‘anticorrelate’ across the tubes. A similar behaviour has been observed in Ar filled nanotubes.[11] The line-scans confirm that nitrogen was indeed encapsulated within the hollow cores and not only concentrated within the walls as observed in previous studies.[13,14] Approximately 10–35% of the tubes investigated appeared to be filled with nitrogen gas. In addition, elemental mapping using EELS (not shown here) revealed that N was localised in pockets (consistent with the compartmentalized carbon morphologies) within the nanotube cores. From representative EEL spectra, it was estimated that the N content within the empty CN_x nanotubes (without N_2 gas trapped) was *ca.* $\leqslant 5\%$. It is noteworthy that the N encapsulation was stable over several weeks and that the gas-filled tubes were not affected after long dispersion periods in acetone.

Our results demonstrate a single-step pyrolytic route to fill CN_x nanotubes with N gas. We have also shown that CN_x nanotubes and nanofibres can be considered as efficient gas containers owing to the presence of pockets (bamboo-like structures), which ensure the encapsulation of gases. The CN_x structures could also serve as containers in order to study liquefaction of N_2 at low temperatures. To the best of our knowledge, this is the first time that N has been incorporated in nanotubes. These observations pave the way to the fabrication of novel gas storage components using spray pyrolysis.

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Notes and references

1 S. Iijima, *Nature*, 1991, **354**, 56.
2 P. M. Ajayan and S. Iijima, *Nature*, 1993, **361**, 333.
3 N. Grobert, M. Terrones, A. J. Osborne, H. Terrones, W. K. Hsu, S. Trasobares, Y. Q. Zhu, J. P. Hare, H. W. Kroto and D. R. M. Walton, *Appl. Phys. A*, 1998, **67**, 595.
4 M. Terrones, N. Grobert, W. K. Hsu, Y. Q. Zhu, W. B. Hu, H. Terrones, J. P. Hare, H. W. Kroto and D. R. M. Walton, *Mater. Res. Soc. Bull.*, 1999, **24**, 43.
5 S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 159.
6 C. Guerret-Piécourt, Y. Le Bouar, A. Loisseau and H. Pascard, *Nature*, 1994, **372**, 761.
7 J. Sloan, D. M. Wright, H. G. Woo, S. Brown, A. P. E. York, K. S. Coleman, J. L. Hutchison and M. L. H. Green, *Chem. Commun.*, 1999, 699.
8 W. K. Hsu, H. Terrones, M. Terrones, N. Grobert, A. I. Kirkland, J. P. Hare, K. Prassides, P. D. Townsend, H. W. Kroto and D. R. M. Walton, *Chem. Phys. Lett.*, 1998, **284**, 177.
9 A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben, *Nature*, 1997, **386**, 377.
10 C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng and M. S. Dresselhaus, *Science*, 1999, **286**, 1127.
11 G. E. Gadd., M. Blackford, S. Moricca, N. Webb, P. J. Evans, A. M. Smith, G. Jacobsen, S. Leung, A. Day and Q. Hua, *Science*, 1997, **277**, 933.
12 R. Kamalakaran, M. Terrones, T. Seeger, Ph. Kohler-Redlich, M. Rühle, Y. A. Kim, T. Hayashi and M. Endo, *Appl. Phys. Lett.*, 2000, **77**, in press.
13 M. Terrones, Ph. Redlich, N. Grobert, S. Trasobares, W. K. Hsu, H. Terrones, Y. Q. Zhu, J. P. Hare, A. K. Cheetham, M. Rühle, H. W. Kroto and D. R. M. Walton, *Adv. Mater.*, 1999, **11**, 655.
14 M. Terrones, H. Terrones, N. Grobert, W. K. Hsu, Y. Q. Zhu, H. W. Kroto, D. R. M. Walton, Ph. Kohler-Redlich, M. Rühle, J. P. Zhang and A. K. Cheetham, *Appl. Phys. Lett.*, 1999, **75**, 3932.
15 J. Bruley and L. M. Brown, *Philos. Mag. A*, 1989, **59**, 247.