

Nitrogen-containing carbon nanotubes

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Carbon nanotubes containing small amounts of nitrogen are produced by the pyrolysis of aza-aromatics such as pyridine, methylpyrimidine and triazine over cobalt nanoparticles in an Ar atmosphere; good yields of such nanotubes are obtained by carrying out the pyrolysis of a mixture of pyridine and Fe(CO)₅ in flowing Ar + H₂.

Carbon nanotubes are generally prepared by the arc evaporation of graphite¹ or by the pyrolysis of hydrocarbons in the presence of metal particles.^{2,3} Encouraged by the report that nitrogen-substituted C₆₀ has been prepared,^{4,5} we were interested to explore whether carbon nanotubes containing nitrogen

could be prepared by employing appropriate precursor molecules. Nanotubes containing both boron and nitrogen have been grown in the electric arc discharge between graphite cathodes and graphite anodes filled with boron in a nitrogen atmosphere.⁶ Such B_xC_yN_z nanotubes have been recently prepared by the pyrolysis of CH₃CN:BCl₃ at 1220 K over Co powder.⁷ In the present study, we have carried out the pyrolysis of pyridine, 5-methylpyrimidine and *s*-triazine under reductive conditions at high temperatures in the presence of fine Co particles (*ca.* 50 nm diam.). Another strategy that we have employed is to carry out the pyrolysis of pyridine in the presence of Fe(CO)₅, which provides the source of small iron particles for the nucleation and growth of the nanotubes.

The procedure adopted for the pyrolysis of the aza-aromatics was as follows. Argon gas was passed through pyridine or 5-methylpyrimidine at room temperature, and the gas mixture

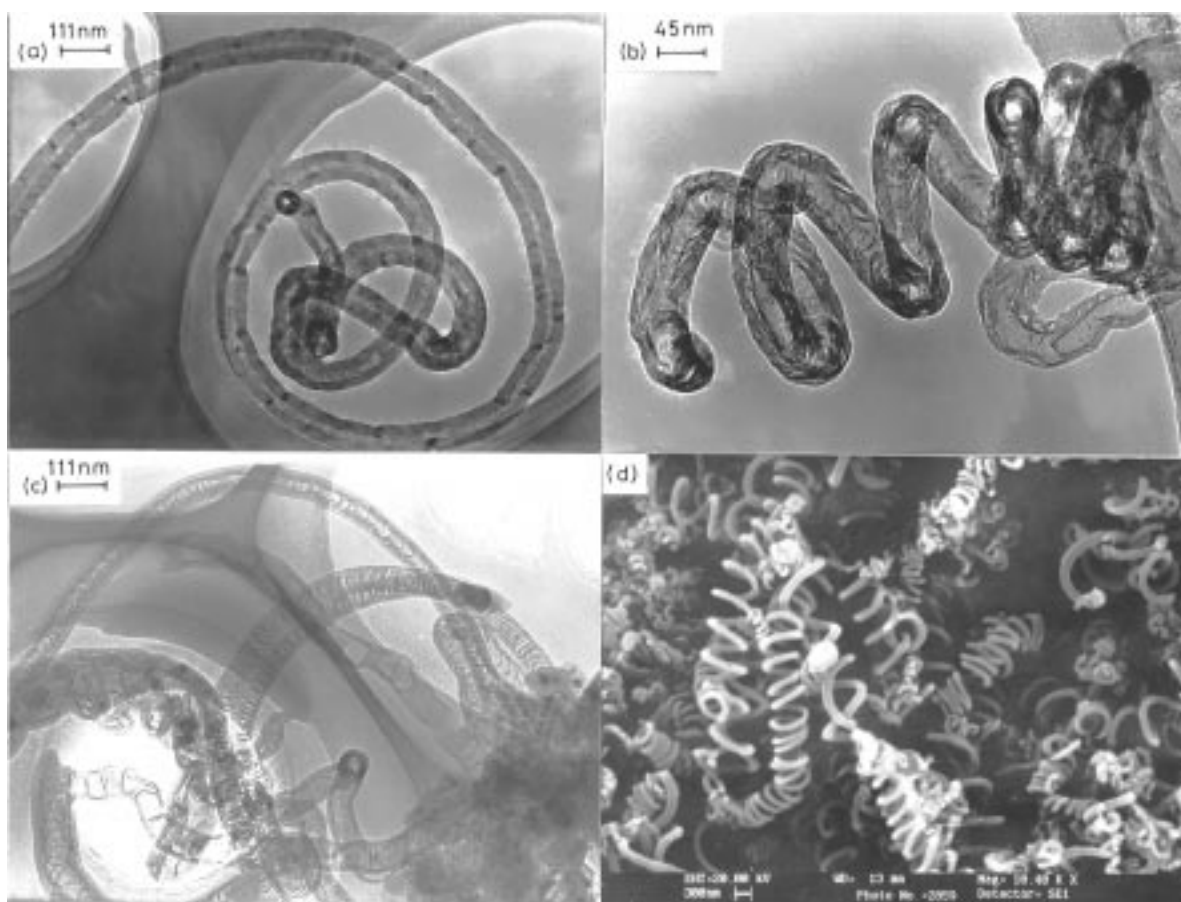


Fig. 1 (a) TEM image of nanotubes obtained by the pyrolysis of pyridine over cobalt powder at 1123 K. In (b) and (c), TEM images of nanotubes obtained by the pyrolysis of *s*-triazine over cobalt powder at 1123 and 1273 K respectively are shown. A SEM image of the nanotubes obtained by the pyrolysis of *s*-triazine over cobalt powder at 1273 K is shown in (d). The coiled nature of the nanotubes can be seen clearly in the images given in (b) and (d).

carrying the vapours of the aza-aromatic was then passed over cobalt nanoparticles (flow rate=50 sccm) placed inside a tubular furnace maintained at the desired temperature. In the case of *s*-triazine, it was sublimed by heating it to 573 K and the vapour then mixed with Ar was passed through the furnace containing the Co powder. Pyrolyses were carried out at 973, 1123 and 1273 K. Pyrolysis of pyridine in an admixture with $\text{Fe}(\text{CO})_5$ was carried out as follows. A measured quantity (0.5 ml) of $\text{Fe}(\text{CO})_5$ was placed in a bubbler near the inlet of a tubular furnace and a mixture of $\text{Ar} + \text{H}_2$ (90% + 10%) containing pyridine vapour was passed through it before its passage through the hot zone of the furnace, which was maintained at 1373 K. The pyrolysis products were examined by elemental analysis and X-ray photoelectron spectroscopy (XPS) using a VG scientific ESCALAB V spectrometer, in addition to recording images by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

In Fig. 1(a) we show a typical TEM image of the nanotubes obtained by the pyrolysis of pyridine at 1123 K over Co powder in an Ar atmosphere. The image clearly shows the cylindrical structure of the nanotubes with a central hollow region, just as in carbon nanotubes. There are, however, some regions with features due to non-cylindrical stacked cones. The stacked cones appear to become more prominent as the nitrogen content of the aza-aromatic increases. Thus, pyrolysis of *s*-triazine at 1123 and 1273 K over Co powder gives rise to nanotubes whose central portion predominantly consists of the stacked cone features as shown in Fig. 1(b) and (c). Such cone-shaped features have been observed by Terrones *et al.* in $\text{B}_x\text{C}_y\text{N}_z$ nanotubes.⁷ An interesting feature of the images of the nanotubes produced from *s*-triazine shown in Fig. 1(b) and (c) is that the nanotubes show a coiled (or spring-like) structure. This is seen clearly in the SEM image shown in Fig. 1(d).

XPS of the nanotubes prepared by the pyrolysis of the aza-aromatics showed the C 1s signal at 285 eV (taking the Cu $2p_{3/2}$ binding energy value at 932.8 eV as reference) which is characteristic of graphitic carbon. The N 1s signal (Fig. 2) showed two distinct features at 398.5 eV and 401 eV in the nanotubes prepared by the pyrolysis at 973 K, the signal at 398.5 eV being characteristic of nitrogen in pyridine. The feature at 401 eV arises from nitrogen atoms present in the graphene sheets.⁸ As the temperature of pyrolysis increases, we notice the gradual disappearance of the feature at 398.5 eV. Thus, at higher temperatures almost all the nitrogen is present inside the graphene sheets. The nitrogen content decreases with increasing the temperature of pyrolysis, but up to *ca.* 1% nitrogen remains even when the pyrolysis is carried out at 1373 K. Based on the XPS band intensities, the C to N ratios in our samples were calculated by taking the ratio of the respective integrated peak areas and by dividing them by the

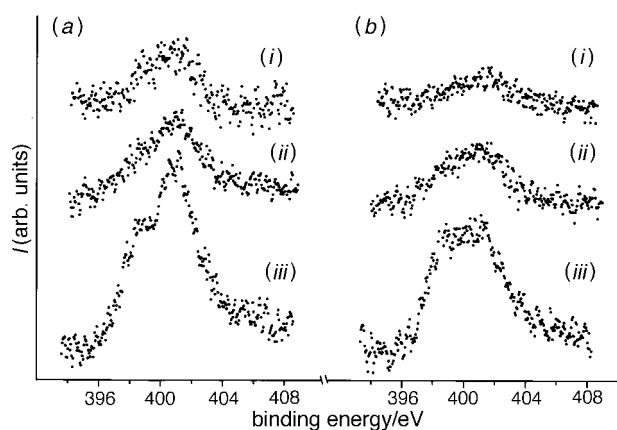


Fig. 2 N 1s signals from nanotubes obtained by the pyrolysis of (a) pyridine and (b) *s*-triazine over Co powder at (i) 1273 K, (ii) 1123 K and (iii) 973 K

photoionization cross-section ratios for the 1s level.⁹ We estimate the nitrogen content to be around 5%, 3.5%, and 3% in the nanotubes prepared by the pyrolysis of pyridine at 973, 1123 and 1273 K respectively. The nitrogen content (as obtained from XPS data) is somewhat lower in the nanotubes obtained by the pyrolysis of *s*-triazine (4.5% and 1% respectively for pyrolysis carried out at 973 and 1273 K). Elemental analysis of the nanotubes obtained by the pyrolysis of the aza-aromatics at 1273 K reproducibly gave *ca.* 1% nitrogen. However, this analysis would be erroneous due to the presence of other graphitic species in addition to nanotubes, although the results clearly establish the presence of nitrogen in the nanotubes. The presence of nitrogen was further confirmed by electron energy loss spectroscopy (EELS) analysis carried out with TEM.

We have been able to obtain excellent yields of nitrogen-containing nanotubes, nearly free of other graphitic species, by carrying out the pyrolysis of pyridine in the presence of $\text{Fe}(\text{CO})_5$. Our earlier experiments on the pyrolysis of benzene in the presence of $\text{Fe}(\text{CO})_5$ at 1173 K in a 85% Ar–15% H_2 mixture gave good yields of carbon nanotubes.¹⁰ In this procedure, the iron particles formed by the decomposition of $\text{Fe}(\text{CO})_5$ act as nucleating centres for the growth of the carbon nanotubes. We show the SEM image of the nanotubes obtained by the pyrolysis of pyridine in an admixture with $\text{Fe}(\text{CO})_5$ at 1373 K in a 90% Ar–10% H_2 mixture (total flow rate=1000 sccm) in Fig. 3(a). The nanotube structure is similar to that obtained by the pyrolysis of pyridine over cobalt powder as can be seen from the TEM image in Fig. 3(b). XPS analysis

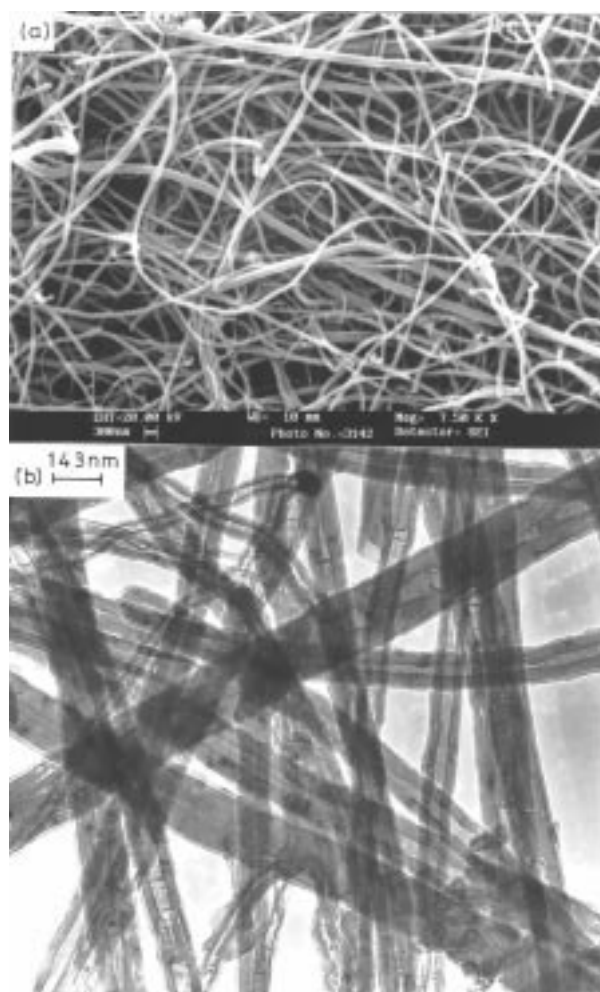


Fig. 3 (a) SEM and (b) TEM images of nanotubes obtained by the pyrolysis of pyridine with $\text{Fe}(\text{CO})_5$ at 1373 K in a 90% Ar–10% H_2 mixture

shows the nitrogen content of these nanotubes to be *ca.* 2%; this was also confirmed by elemental analysis.

Assuming that the nanotubes obtained by us from the pyrolysis of the aza-aromatics around 1273 K contain at least 1–2% nitrogen, the average composition works out to be between C₅₀N and C₁₅₀N. The nitrogen content of the nanotubes is clearly low, but the problem remains as to the manner in which the nitrogen atoms are bonded to the carbons. We were not able to establish the nature of the nitrogen–carbon bonds in these nanotubes, but it is possible that the nitrogen (sp³) is accommodated as part of a five-membered ring. The XPS results are, however, consistent with sp² nitrogen atoms being present in the graphene sheets,⁸ possibly at the edges or in the cone-shaped features. It is noteworthy that the nanotubes prepared recently by the pyrolysis of acetonitrile over carbon coated cobalt powder at 1273 K in an Ar atmosphere also contained some nitrogen.¹¹ Similarly, the nanotubes produced by the pyrolysis of 2-amino-4,6-dichloro-*s*-triazine over thin films of cobalt at 1223 K contain a finite amount of nitrogen, shown by the weak EELS signal.¹² The nitrogen content is somewhat greater in B_xC_yN_z nanotubes where we find the content of boron to be nearly equal to that of nitrogen.¹³

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