Functionalised carbon nanotubes from solutions

C. N. R. Rao,* A. Govindaraj and B. C. Satishkumar

CSIR Centre of Excellence in Chemistry and Solid State & Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Refluxing carbon nanotubes in H_2SO_4–HNO_3 results in a clear colourless solution which on removal of the solvent gives a white solid containing functionalised nanotubes; neutralization of the acidic solution results in the precipitation of a brown solid containing nanotubes.

Carbon nanotubes which are uncapped upon treatment with boiling nitric acid or other oxidants are known to contain hydroxy and carboxylic groups,[1–4] but the nanotubes retain their essential structural features during the oxidation process. In an effort to prepare carbon nanotubes containing a high proportion of acidic functional groups, we refluxed a known quantity of multi-walled carbon nanotubes with H_2SO_4–HNO_3 (3 : 2 by volume) for 2 h to obtain a clear colourless solution. Removal of the solvent and the excess acid from this solution under vacuum gave a white solid residue, in contrast to the black nanotubes that we started with. The white solid was washed extensively with distilled water and dried before subjecting it to various investigations.

Scanning electron micrographs (recorded with a LEICA S440i microscope) of the white solid show the presence of nanotube like structures (Fig. 1). The nanotubes are clearly seen in the transmission electron microscope images (recorded with a JEOL JEM-200CX microscope). Some of the nanotubes are isolated, but most of them appear to be present as aggregates. Fig. 2 shows typical TEM images of the nanotube structures found in the white solid. The images do not clearly reveal the graphitic fringes, possibly because of extensive functionalisation of the nanotubes. Acid–base titrations indeed showed that there were 10^{21} acidic sites per gram in the white solid, much higher than in nanotubes uncapped by oxidants such as HNO_3.

The C 1s core-level spectrum of the white solid (recorded with a VG ESCALAB spectrometer) does not show the $\pi \rightarrow \pi^*$ shake-up satellite [Fig. 3(*a*)], indicating the absence of extended conjugation which is found in the parent nanotubes. The core-level spectrum also shows evidence for sulfur and oxygen, the surface concentrations of carbon, oxygen and sulfur being in a 2 : 5 : 1 ratio, pointing to the presence of SO_3H, OH and other groups. The IR spectrum shows characteristic bands due to OH (3300 cm^{-1}), SO_3H (1050, 1170, 1350 cm^{-1}) and C=C/C=O (1600 cm^{-1}) groups. The ^{13}C NMR spectrum of the solid (recorded with a Bruker MSL-300 spectrometer) shows a broad signal centred at δ *ca.* 145, compared to δ 130 of the parent nanotubes [Fig. 3(*b*)]. Such a downfield shift can arise from the presence of OH and SO_3H groups. The solid however comprises

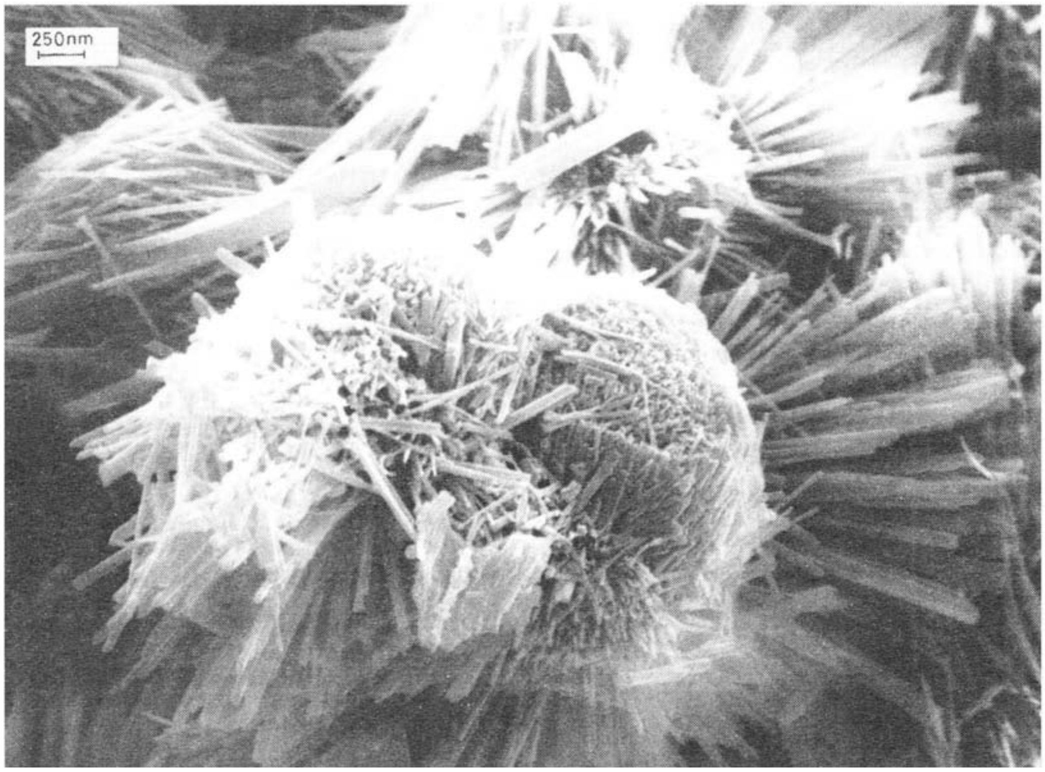

Fig. 1 A typical SEM image of the white solid obtained from the acidic solution of nanotubes

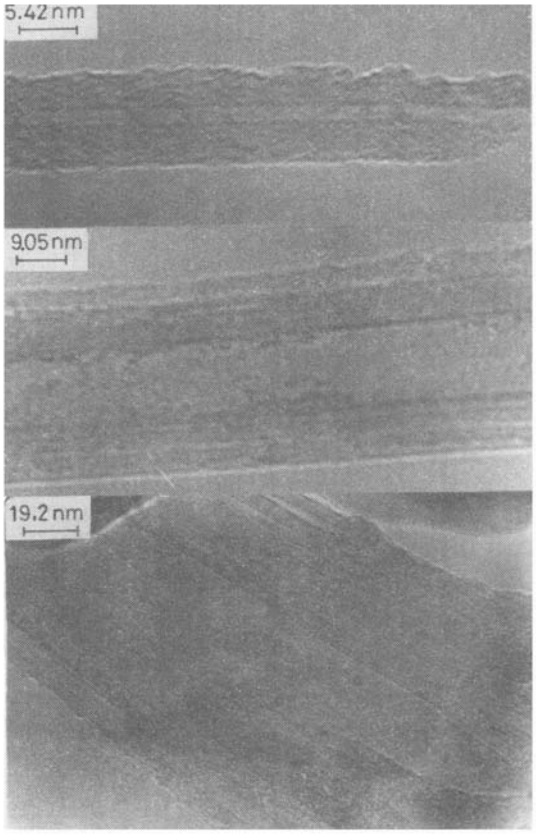

Fig. 2 TEM images of the white solid obtained from the acidic solution of nanotubes

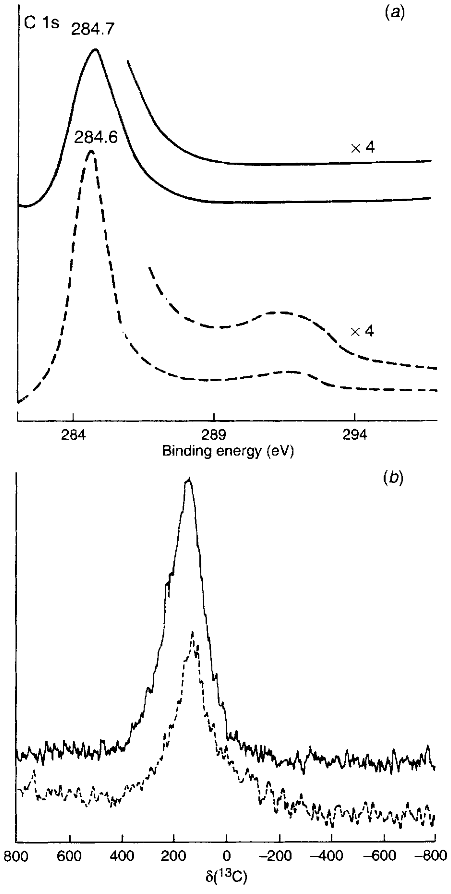

Fig. 3 C 1s spectra (*a*) and ^{13}C NMR (7.05 T, 75.467 MHz) spectra (*b*) of the white solid obtained from the acid solution of nanotubes (—) and of the parent carbon nanotubes (---)

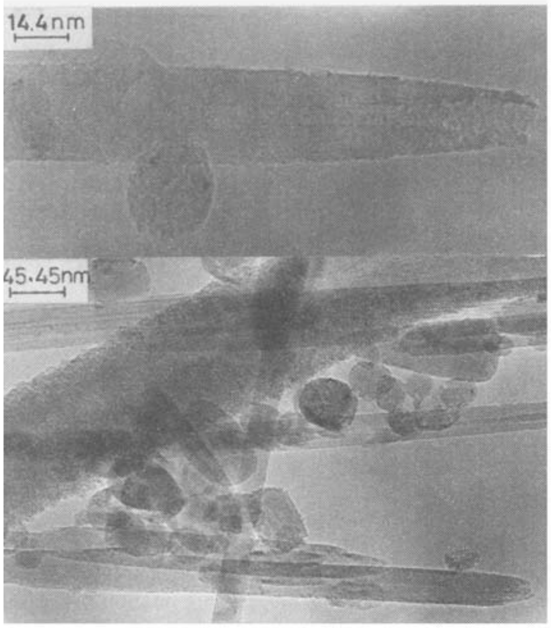

Fig. 4 TEM images of the light brown solid obtained by neutralizing the acid solution of nanotubes with alkali

isolated or conjugated C=C bonds, since there is no evidence for the presence of a large proportion of sp^3 carbons in the NMR spectrum. The powder X-ray diffraction pattern (recorded with Cu-Kα radiation) of the white solid exhibits a relatively intense (002) reflection at a somewhat smaller angle (2θ = 25.22°) than the parent nanotubes (2θ = 25.73°) indicating a slight expansion of the spacing between the graphitic sheets. These characterization studies are consistent with the preponderant presence of functionalised nanotubes in the white solid.

On neutralising the acid solution of the nanotubes with NaOH, a light brown solid is gradually formed. The IR spectrum of this solid has sharp features due to OH (3450 cm^{-1}), SO_3 (1100–1230 cm^{-1}) and C=C/C=O (1680 cm^{-1} groups. The TEM images of the brown solid show the presence of nanotubes with a higher proportion of well separated tubes (Fig. 4). It appears that the presence of SO_3H groups in the white solid gives rise to a greater association of the nanotubes.

The observation of functionalised nanotubes in the solids extracted from acid solutions is of considerable interest. This could lead to a study of their possible uses and of their transformations. It is indeed remarkable that such large structures of carbon (a micron or more in length) remain in the solution phase and are regenerated in the solid state upon removal of the solvent.

We thank the Jawaharlal Nehru Centre for Advanced Scientific Research for the use of some of the facilities.

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Received, 6th February 1996; Com. 6/00854B