

EXPERIMENTAL MEASUREMENTS OF NITROGEN ADSORPTION IN CARBON NANOTUBES

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Introduction

Since their discovery in 1991 [1], carbon nanotubes have been the subject of a considerable amount of research from both a fundamental and an applied perspective. Carbon nanotubes present narrow channels in the centre and it was speculated that it could be possible to store atoms in these cavities. One highlight of this work to date is the demonstration that tubes can be opened [2] and therefore filled. In this context, both theoretical [3, 4] and experimental [5] studies have been carried out in order to determine the suitability of carbon nanotubes for gas storage.

Generically two distinct types of carbon nanotubes exist, depending on whether the tube walls are made of one layer (single-walled nanotubes: SWNT) or more than one layer (multi-walled nanotubes: MWNT). MWNT are usually produced by electric-arc discharge between two graphite electrodes in an helium atmosphere, while SWNT are prepared using the same method by simply introduce catalyst species in the anode. Modified version of the arc discharge method is used to make doped multi-walled nanotubes with boron (BC nanotubes [6]) in which BC_3 domains are incorporated in the hexagonal carbon network. The benefit of boron doping is that it assists the graphitization process and favours the increasing of the average length of the nanotubes. However, whatever the method used for the synthesis of nanotubes, the samples obtained are not pure. Recently a new development in the nanotubes forms has lead to the preparation of packed nanotubes in films [7]. Here we report a systematic study of nitrogen adsorption on different kind of carbon nanotubes prior to their evaluation as gas storage media.

Experimental

Three samples have been received for investigation: MWNT, which were made by the arc discharge method, BC made by the arc discharge method by using a BC composite anode and a graphite cathode (both of these samples have been provided by W. Hsu *et al.* from the University of Sussex, UK) and SWNT originating from an arc discharge experiment using a mixture Ni/Y as a catalyst material in the graphite anode (sample provided

by W. Maser *et al.* from the CSIC in Zaragosa, Spain). SWNT can be found in a spongiform “collaret” around the cathodic deposit and in carbonaceous webs that extend from the cathode to the reactor walls. The samples were characterised by scanning electron microscopy (SEM JEOL 6310), transmission electron microscopy (TEM JEOL 2000FX) and nitrogen adsorption at 77 K. Prior to gas adsorption, the samples were degassed at 10^{-3} bar at 200 °C for 24 hours. Nitrogen isotherms at 77 K were measured using a volumetric adsorption apparatus (ASAP 2010, Micromeritics Instrument Corporation).

Results and Discussion

SEM images show the light and porous aspect of the collaret for the SWNT (curved fibril structures crossing each other can be observed) and that the supplied MWNT and BC nanotubes consist of balls of loosely aggregated nanotubes. Table 1 summarised the observations of the different nanotubes samples made by TEM. HRTEM observations show that the SWNT are made of bundles of few tens SWNT arranged in a triangular lattice having a parameter of about 17 Å. All the nanotubes samples are closed.

Nitrogen adsorption measurements at 77 K were made on the as received nanotubes without further purification. The isotherms obtained on the different samples are shown in Figure 1. We have seen no differences between the SWNT coming from the webs or the collaret in terms of nitrogen adsorption. According to the IUPAC classification, the isotherms are of mixed type I (at low relative pressures)/II (at medium relative pressure), indicating the presence of a certain amount of microporosity as well as the development of mesoporosity, especially for the SWNT sample. No hysteresis loop closure can be clearly observed: this indicates that some nitrogen is retained within the nanotube structures. In Table 2 are listed the BET surface areas and micropore volumes according to the Dubinin-Asthakov method [8] of the different nanotubes samples. The MWNT and BC samples exhibit very low surface areas, while the surface area of the SWNT is consistent with the external surface area calculated for bundles of SWNT (Table 1). Although some studies [4, 5] suggest the potential of carbon nanotubes as

adsorbents, nitrogen adsorption experiments on nanotubes presented here and published so far [9, 10] show very low surface areas from 10 to 300 m² g⁻¹ even on opened tubes [10]. These values are far less than the surface areas of typical activated carbon used for gas storage which approach 1500 m² g⁻¹.

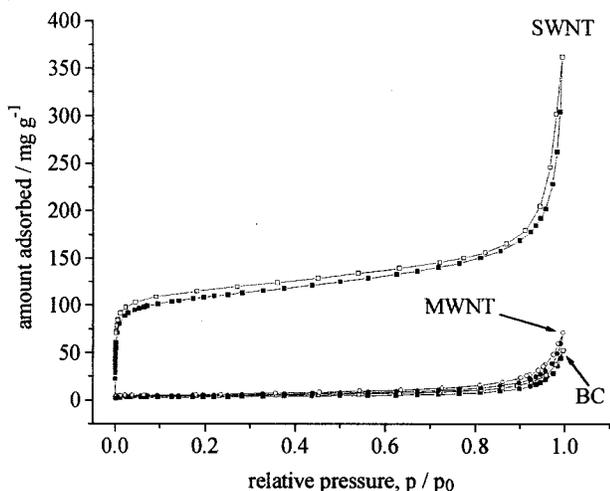


Figure 1. Nitrogen isotherms at 77 K for MWNT, BC tubes and SWNT.

Conclusions

Nitrogen adsorption in carbon nanotubes depends on their structure and their configuration: differences exist between MWNT and SWNT. In order to access the hollow centre of the tubes, further work needs to be done to open the closed tubes. As far as nitrogen adsorption is concerned, the potential of carbon nanotubes as gas storage media remains uncertain.

References

1. Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991; 354 (7): 56-58.

2. Tsang SC, Harris PJF and Green MLH. Thinning and opening of carbon nanotubes by oxidation using carbon dioxide. *Nature* 1993; 362 (8): 520-522.

3. Wang K and Johnson JK. Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealised carbon slit-pores. *J. Chem. Phys* 1999; 110 (1): 577-586.

4. Stan G and Cole MW. Hydrogen adsorption in nanotubes. *J Low Temp Phys* 1998; 110 (112): 539-544.

5. Dillon AC, Jones KM, Bekkedahl TA, Kiang CH, Bethune DS and Heben MJ. Storage of hydrogen in single-walled carbon nanotubes. *Nature* 1997; 386 (27): 377-379.

6. Carroll DL, Redlich P, Blasé X, Charlier JC, Curran S, Ajayan PM, Roth S, Ruhle M. Effects of nanodomain formation on the electronic structure of doped carbon nanotubes. *Phys Rev Lett* 1998; 81 (11): 2332-2335.

7. Shaffer MSP, Fan X and Windle AH. Dispersion and packing of carbon nanotubes. *Carbon* 1998; 36 (11): 1603-1612.

8. Gregg SJ and Sing KSW, *Adsorption, Surface Area and Porosity*, 2nd Ed., London, New York, Paris, Tokyo, Toronto, Academic Press, 1982.

9. Mackie EB, Wolfson RA, Arnold LM, Lafdi K and Mignone AD. Adsorption studies of methane films on catalytic carbon nanotubes and on carbon filaments. *Langmuir* 1997; 13 (26): 7197-7201.

10. Gaucher H, Grillet Y, Beguin F, Bonnamy S and Pellenq RJM. Low temperature physical adsorption in well-defined multiwall carbon nanotubes. *Fundamentals of Adsorption 6*. Ed F. Meunier 1998: 243-248.

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Table 1. Characteristics of the different nanotubes samples obtained using TEM.

	MWNT	SWNT	BC
Diameter	3-40 nm	Bundle: 5-20 nm SWNT: 1.4 nm	10-50 nm
Length	3-20 μm	>10 μm	10-80 μm
Tips	Closed	Assumed to be closed	Closed

Table 2. Data from nitrogen adsorption at 77 K

	BET surface area / m ² g ⁻¹	DA micropore volume / cm ³ g ⁻¹
MWNT	15	0.006
BC	10	0.004
SWNT	302	0.142