POROSITY OF CARBON NANOTUBES

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Introduction

Recent developments in the synthesis of carbon nanotubes have opened up the possibility for new applications of these materials in some areas of adsorption and catalysis. In this paper we will discuss the characterization of both single and multiwalled nanotubes by nitrogen adsorption and the differences in porosity of the two materials. We have also investigated the use of adsorption as a tool for determining the purity of multiwalled carbon nanotube samples.

Experimental

Single wall nanotubes (SWNTs) were manufactured by Carbolex Inc. using the electric arc method with a Ni/Y catalyst They were purified by refluxing in 2M nitric acid for 24 hours, filtered and then sonicated in DMSO for 12 hours before drying. Multiwalled nanotubes (MWNTs) were produced at the CAER by the catalytic decomposition of a ferrocene-xylene mixture at about 700°C and atmospheric pressure, as described elsewhere[1]. Scanning electron microscopy (SEM) was used to estimate the purity of the MWNT samples. The as-produced samples contain about 5% iron. One of the samples was leached in HCl acid to attempt to remove the iron. Nitrogen adsorption isotherms were obtained at 77K using an automated adsorption analyzer, OMNISORP 610. The mesopore volume, surface area and pore size distributions were calculated using the BJH method[2]. The micropore volume was determined by subtraction of the mesopore volume from the total pore volume.

Results and Discussion

Adsorption isotherms of SWNT and MWNT are compared in Figure 1. The MWNT sample is ~100% purity as determined by SEM. The adsorption isotherms for both samples are type 4 isotherms which are typical of mesoporous carbons, with the MWNT giving considerably higher nitrogen adsorption. The mesopore size distributions of the two samples are shown in Figure 2. The multiwalled sample clearly has a higher mesopore volume, and the average size of the pores is ~ 3.5 nm. This value corresponds approximately to the diameter of the central core of the MWNTs as determined by transmission electron microscopy which showed it to be in the range of 3-7 nm, Figure 3. Other adsorption data has shown that the average pore diameter of MWNTs is 4-6 nm [3]. The calculated mesopore volumes of MWNTs and SWNTs are shown in Table 1. The SWNT has a mesopore volume of 0.05 cc/g while that of the pure MWNT sample is about 0.45 cc/g.

Observations by SEM have shown that small iron particles are present at the ends of the tubes, as a consequence of their catalyzing nanotube growth,. They are also located intermittently along the innermost tube. Leaching with HCl removed about 50% of the iron catalyst. The acid treatment probably improves access to the core of the MWNTs by removing iron from the ends. Even though the total mesopore volume is not significantly enhanced, Table 1, it does seem to broaden the mesopore size distribution slightly.

Nitrogen adsorption may also prove to be a useful tool for estimating the purity of MWNTs (to distinguish other forms of carbon that are co-produced). The curves in Figure 4 were obtained for MWNT samples of different purities (as estimated by SEM). The higher purity materials have much narrower pore size distributions than those containing more appreciable quantities of other carbon structures.

Table 1: Mesopore volume of different nanotube samples.

Sample ID	purity (% MWNTs)	Mesopore volume (cc/g)
SWNT	~100%	0.05
MWNT-A	~95%	0.47
MWNT-B	~100%, leached	0.48
MWNT C	~90%	0.27
MWNT D	~80%	0.10

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References

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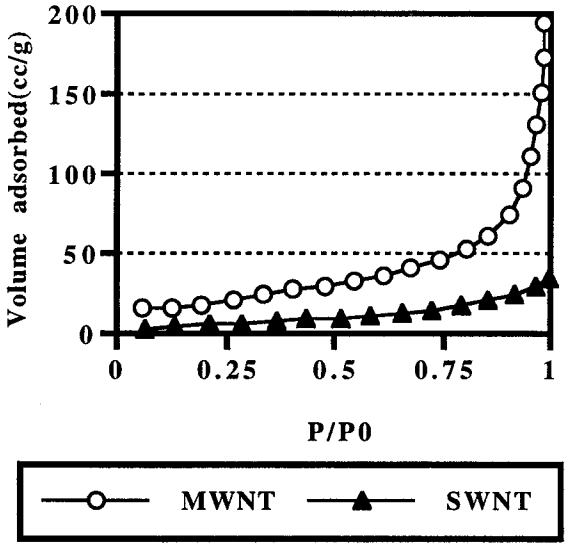

Figure 1: N_2 adsorption isotherm of SWNT and MWNT.

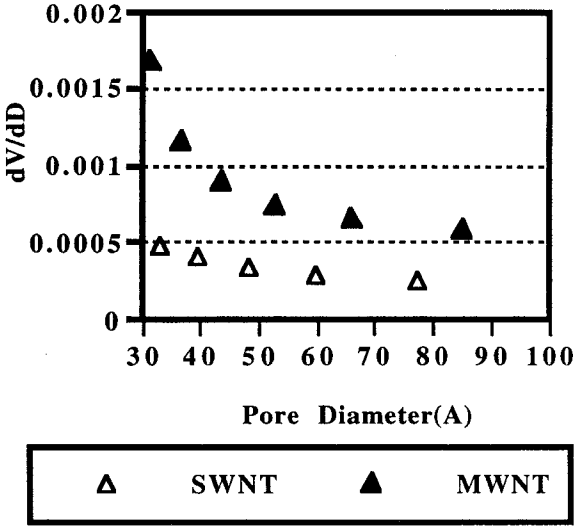

Figure 2: BJH mesopore size distribution of SWNT and MWNT samples.

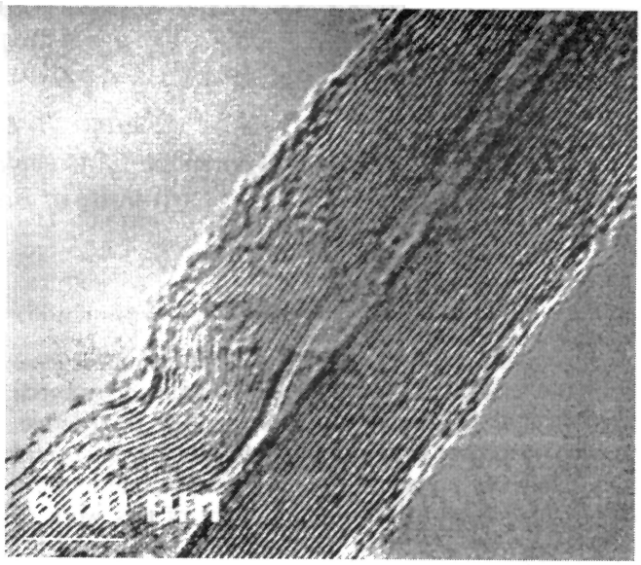

Figure 3: TEM micrograph of MWNT

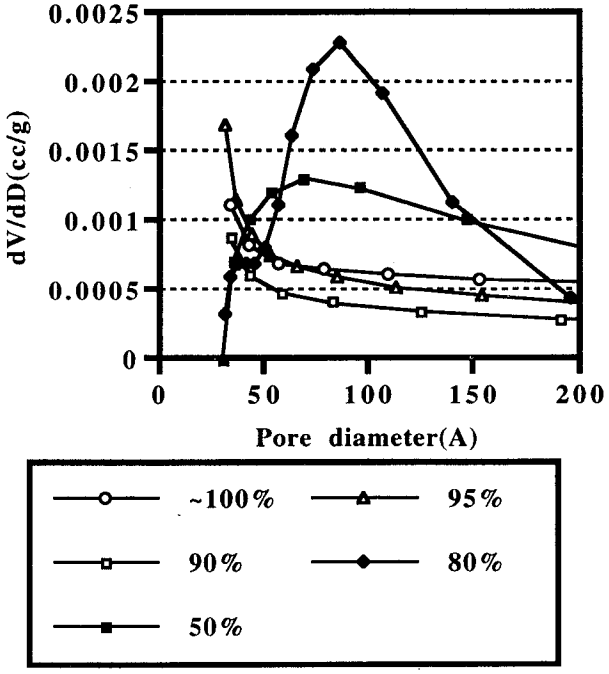

Figure 4: BJH mesopore size distribution of MWNT samples of different purities.