

VARIABILITY IN CHARACTERIZATION RESULTS OF SINGLE-WALLED CARBON NANOTUBES

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Introduction

A wide range in adsorption surface areas (150-1500 m²/g) [1] has been reported for single walled carbon nanotubes (SWNTs) for which the most obvious reason is diversities in sample purity and the structure of nanotubes. However, we have discovered that slight changes in measuring N₂ adsorption data using conventional techniques and the sample age could also affect the characterization results.

Experimental

Purified SWNT samples that contained 95-98 wt% electric arc (EA) produced (EA95), and ~80 wt% and ~95 wt% HiPco produced (CVD80 and CVD95) SWNTs were selected to reflect the properties of nanotubes (and not impurities) as a function of manufacturing process. The characterization techniques included X-ray diffraction (XRD, $\lambda = 0.154$ nm) for analysis of SWNT structure, N₂ adsorption at 77K for determining adsorption surface area, porosity and pore size distribution (PSD), and thermogravimetric analyzer coupled with a mass spectrometer (TG-MS) for analysis of SWNT surface chemistry.

Results and Discussion

The XRD results showed a clear difference between EA and HiPco samples (Fig.1a). The EA sample exhibited two sharp peaks corresponding to the presence of well-defined structures.

The 1.47 nm peak (site 1, Fig.1b) represents the diameter of SWNTs in a heterogeneous SWNT bundle. The 0.34 nm peak corresponds to the average size of grooves present on the periphery of SWNT bundles (site 3, Fig.1b). Sample CVD80, however, did not exhibit peaks corresponding to sites 1 and 3, which is most likely due to presence of inferior quality of SWNTs (i.e. gross structural defects) produced by a low temperature CVD process [2].

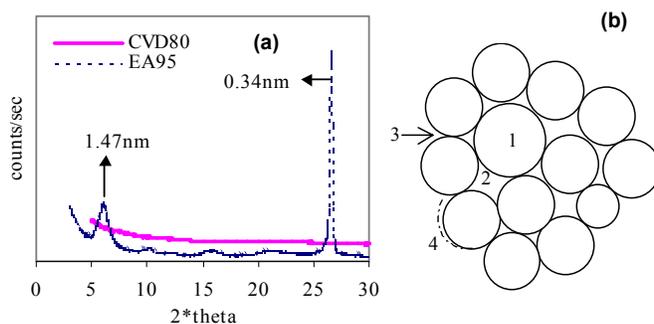


Fig.1. (a) XRD of SWNT samples (b) structural depiction of four adsorption sites on a bundle of SWNTs

The samples EA95 and CVD80 were also analyzed by N₂ adsorption at 77K. The typical procedure for N₂ adsorption requires outgassing of a sample (10 milli torr) at 140°C to desorb moisture. For freshly produced (< 1 month aged) SWNTs, increasing the

outgassing temperature from 140°C to 340°C increased the N₂ adsorption capacities for both, EA and HiPco, SWNT samples (Fig.2a). Oxidative purification processes are known to open the otherwise close-ended SWNTs [3]. The dangling carbon bonds generated in the process are most likely saturated with carboxylic (-COOH) groups, which can be removed by subjecting nanotubes to high temperatures [4]. In fact, decomposition of acidic functional groups on carbon blacks is known to occur at temperature as low as 200-300 °C [5, 6, 7]. It is very likely that the purified SWNT samples EA95 and CVD80 could have contained some open-ended SWNTs that were blocked by functional groups. Increasing the outgassing temperature from 140°C to 340°C could have removed some of these functional groups, thus, increasing the availability of nanotubes' porosity.

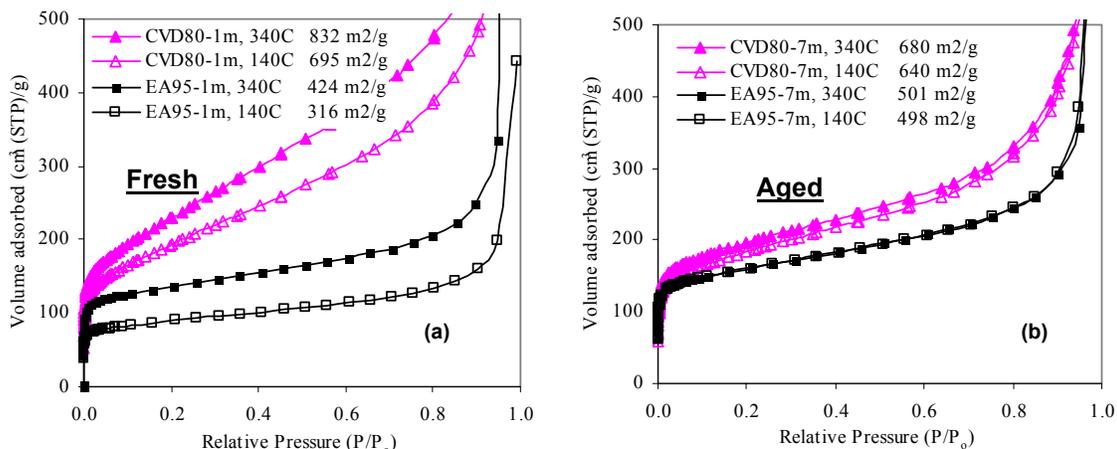


Fig.2. Effect of outgassing temperature on (a) < 1 month and (b) 7 month aged SWNT samples

The effect of increased N₂ adsorption capacity with increased outgassing temperature, however, could not be observed for aged (7 months aged) SWNT samples. Both, EA and HiPco, samples seemed inert to such changes (Fig.2b). Additionally, the N₂ adsorption surface area (and capacities) for aged samples was different from those obtained under similar conditions for the fresh (< 1 month aged) samples. This suggested that the aging of SWNTs affected their adsorption properties.

The differences in characterization results were also recognized in the PSDs of sample EA95, as measured by the DFT models (Fig.3). The PSD based on slit pore geometry showed sharp peaks at 5 Å and 12 Å, which could be related to the XRD results (Fig.1a). However, the PSD based on cylindrical pore geometry exhibited peaks at 12 Å and 18 Å, and no peak at 5 Å. The actual geometry of SWNTs contains both, cylindrical and slit, shaped adsorption sites (Fig.1b). A more accurate PSD model that would account for both pore types is required for analysis of pore structures in SWNTs.

Since, the observed increases in N₂ adsorption on fresh SWNTs could have occurred due to changes in surface functionality, it is speculated that “aging” of SWNTs is also a result of changes in functionality of SWNTs. TG-MS analysis for the fresh (< 1 month

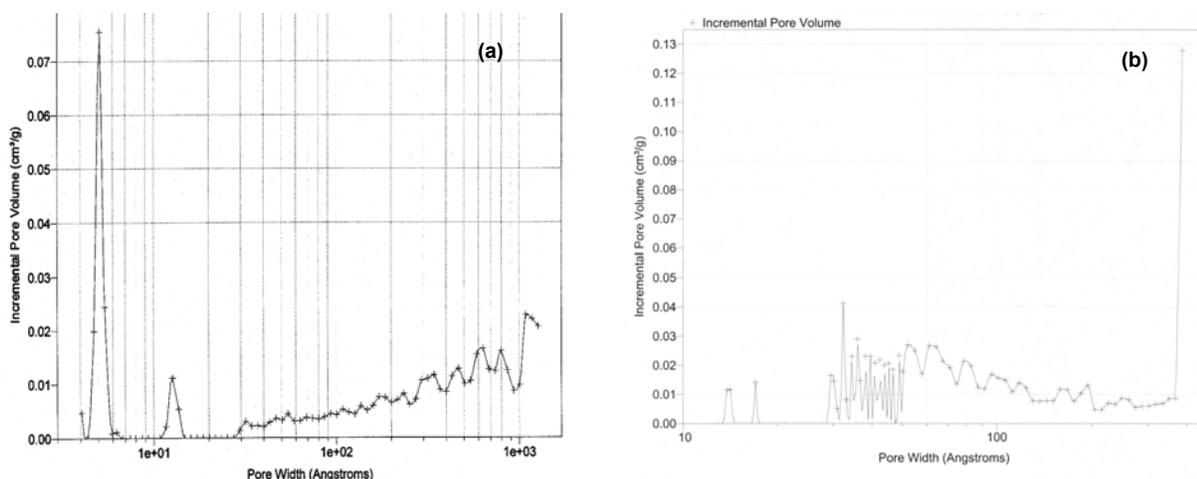


Fig.3. PSD calculated by DFT model based on (a) slit pore (b) cylindrical pore geometry for sample EA95-7m, 140C

aged) and aged (7 months aged) HiPco sample, CVD95 (Fig.4) revealed that for the fresh sample, H₂O, CO and CO₂ were released. However, for the aged sample only H₂O and CO were released. If during aging, some carboxylic groups were converted to carbonyls (e.g. -COO + C → 2 -CO), this could explain the release of CO from the aged sample. However, more work is warranted to quantify the temporal changes in surface functionality of SWNTs.

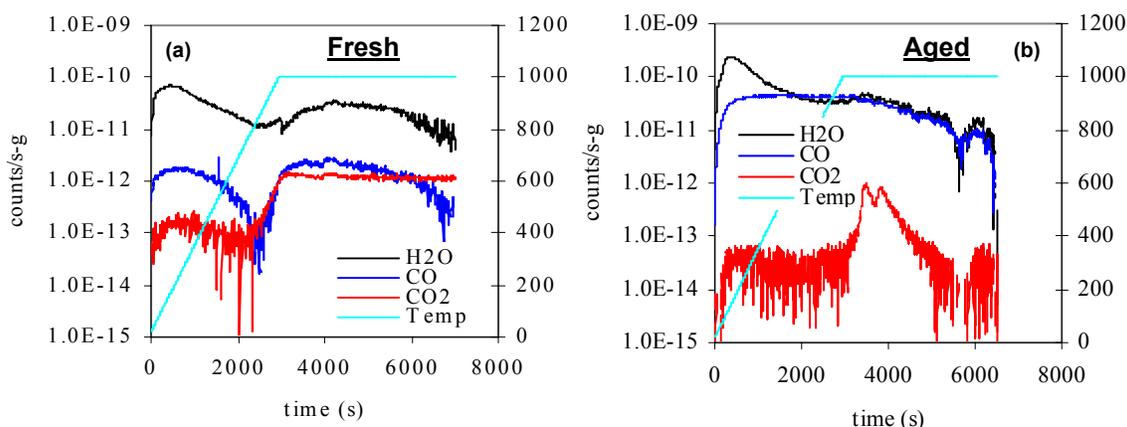


Fig.4. TG-MS results for (a) fresh and (b) 7 months aged sample CVD95

Conclusions

The reported data showed that slight changes in conventional experimental procedures (such as, increase in outgassing temperature prior to N₂ adsorption, choice of pore geometry for determining PSD) and the sample age at the time of analysis affected the characterization results of SWNTs studied in this research. The phenomenon of “aging” appeared to be a dominant factor influencing the N₂ adsorption properties and the surface functionality of SWNTs. The information presented here should alert carbon researchers to consider aging as a parameter when characterizing SWNTs.

References

- [1] Cinke M, Li J, Chen B, Cassell A, et al. Pore structure of raw and purified HiPco single-walled carbon nanotubes. Chemical Physics Letters 2002; 365:69-74.
- [2] Dresselhaus MS, Dresselhaus G, Avouris Ph. Carbon nanotubes: synthesis, structure, properties and applications. Topics in Applied Physics 80. Springer 2000.
- [3] Fujiwara A, Ishiji K, Suematsu H, Kataura H, et al. Gas adsorption in the inside and outside of single-walled carbon nanotubes. Chemical Physics Letters 2001; 336(3):205-211.
- [4] Mawhinney DB, Naumenko V, Kuznetsova A, Yates (Jr) JT, et al. Surface defect site density on single-walled carbon nanotubes by titration. Chemical Physics Letters 2000, 324(1):213-216.
- [5] Puri BR, Bansal RC. Studies in surface chemistry of carbon blacks. Part I. high temperature evacuations. Carbon 1964; 1(4):451-455.
- [6] Barton SS, Gillespie DJ, Harrison BH. Surface studies of carbon: acidic oxides on spheron 6. Carbon 1973; 11(6):649-654.
- [7] Barton SS, Gillespie DJ, Harrison BH. The structure of acidic surface oxides on carbon and graphite—II. Carbon 1978; 16(5):363:365.