

CHARACTERIZATION OF SINGLE-WALLED CARBON NANOTUBES FOR ENVIRONMENTAL IMPLICATIONS

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Abstract

Adsorption capacities of N₂ and various organic vapors on select electric- arc and HiPco produced SWNTs were experimentally measured at 77 K and 298 K, respectively. The results indicated that the amount of N₂ adsorbed on a SWNT sample depended on the sample purity, methodology and on the sample age. Adsorption capacities of organic vapors (100 - 10000 ppmv) on SWNTs in humid conditions were much higher than those for microporous activated carbons. These results establish a foundation for additional studies related to potential environmental applications of SWNTs.

Introduction

A wide range in adsorption surface areas (150-1500 m²/g) [1, 2] 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. Previously we reported that slight changes in measuring N₂ adsorption data using conventional techniques and the sample age could also affect the characterization results [3]. Also, the organic vapor adsorption capacities of SWNTs are generally assumed inferior to those of activated carbons in dry gas streams [9]. Here we report that SWNTs exhibit much higher adsorption capacities for organic vapors than microporous activated carbons in humid gas streams.

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 and porosity, thermogravimetric analyzer coupled with a mass spectrometer (TG-MS) for analysis of SWNT surface chemistry, and gravimetric balance to measure the organic vapor adsorption capacities of the samples.

Results and Discussion

Aging of SWNTs

The XRD results showed differences in morphologies of 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 majority 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 the presence of inferior quality of SWNTs (i.e. gross structural defects) produced by a low

temperature CVD process [2]. Transmission electron microscopy and Raman spectroscopy analyses of these samples showed that sample EA95 contained SWNTs of three different diameters (1.1 nm to 1.52 nm) with majority being 1.52 nm wide [3]. Sample CVD80, on the other hand, was more heterogeneous as it contained five different sized SWNTs (0.9 nm to 11.75 nm) with most nanotubes being 0.9 nm in diameter.

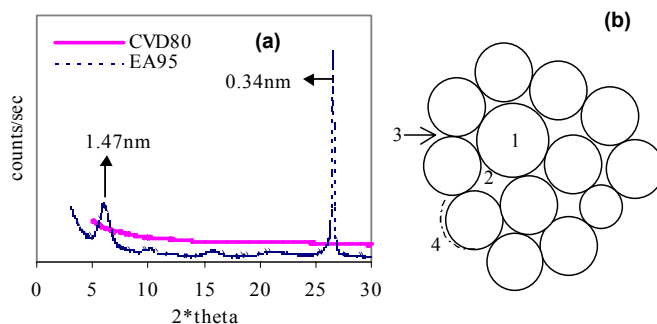


Fig.1. (a) XRD of SWNT samples (b) structural depiction of four adsorption sites on a bundle of SWNTs

The details of the following discussion are presented elsewhere [3], and only a brief description of results is presented for clarity. The surface area and porosity of samples EA95 and CVD80 were measured by N_2 adsorption at 77K. The typical procedure for N_2 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 N_2 adsorption capacities for both, EA and HiPco, SWNT samples (Fig.2a). Oxidative purification processes are known to open the otherwise close-ended SWNTs [4]. 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 [5]. In fact, decomposition of acidic functional groups on carbon blacks is known to occur at temperature as low as -200 - 300°C [6, -8]. Therefore, it is very likely that the purified SWNT samples EA95 and CVD80 contained some open-ended SWNTs that were blocked by functional groups, and increasing the outgassing temperature from 140°C to 340°C removed some of these functional groups, and thus, increased the *availability* of nanotubes' porosity.

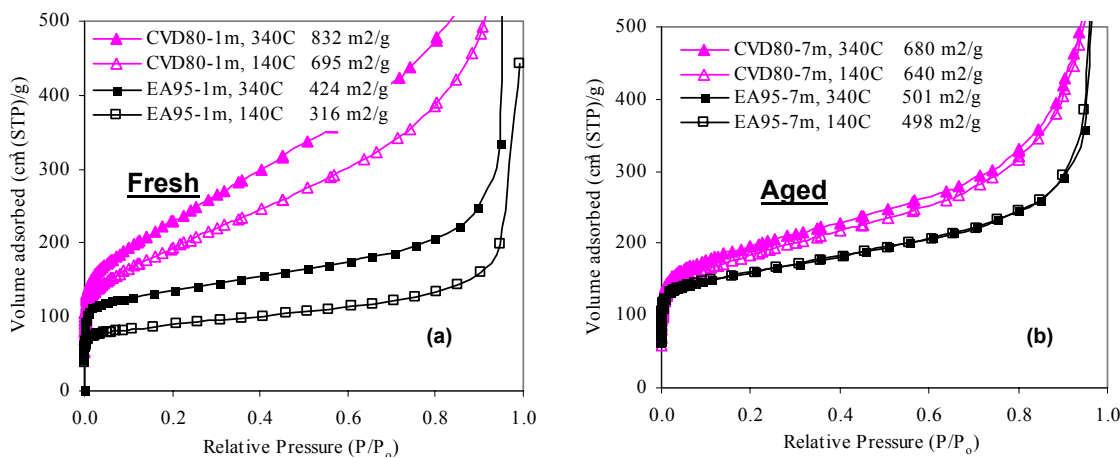


Fig.2. Effect of outgassing temperature on (a) < 1 month and (b) 7 month aged SWNT samples

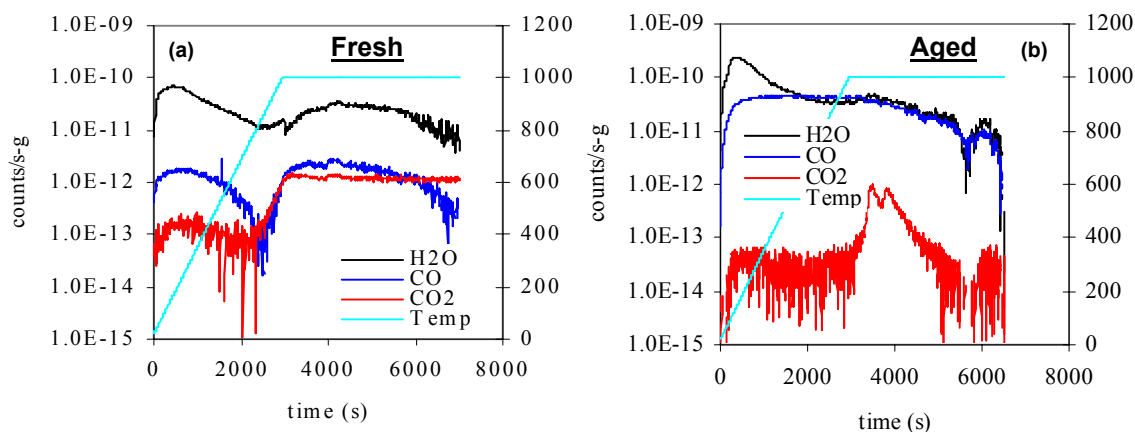


Fig.3. TG-MS results for (a) fresh and (b) 7 months aged sample CVD95

The effect of increased N_2 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 N_2 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. Since, the observed increases in N_2 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 of a freshly (sample age < 1 month) produced and aged (sample age ~ 7 months) HiPco samples (sample CVD95) was performed to gain some insight into the role of nanotube surface chemistry on temporal changes in N_2 adsorption properties (Fig. 3). Surface functionality of nanotubes, as measured by release of H_2O , CO and CO_2 , changed with sample age. The fresh CVD95 sample released H_2O , CO and CO_2 as it was heated in N_2 from room temperature to 1000 °C. However, for the aged sample, only H_2O and CO were released. It is hypothesized that during aging, some carboxylic functional groups were converted to carbonyls (e.g. $-COO + C \rightarrow 2 -CO$).

Interestingly, aging did not exhibit any effects on N_2 adsorption properties of sample CVD95. Since sample CVD95 was more pure than sample CVD80, it is very likely that the purification processes employed for preparation of these samples were different, which could also impacted the surface chemistry of the nanotubes. For example, we observed that sample CVD80, like most SWNTs, was more prone to static electricity than sample CVD95.

Adsorption of Organic Vapors

Previously we reported that organic vapor adsorption capacities of samples EA95 and CVD80 in dry gas streams are inferior to those of microporous activated carbons [10]. We also reported water vapor adsorption isotherms for the same samples [10]. In this study, we measured the organic vapor adsorption capacities of nanotubes using a mixture of ultra high purity N_2 and water vapor (~90% RH) as the carrier gas. The adsorption capacities of samples EA95 and CVD80 were gravimetrically determined for methyl-ethyl ketone (MEK), toluene and cyclohexane vapors individually mixed with the carrier gas. The experimental set up and the methodology was same as that described in reference [11]. The adsorption capacities of

SWNTs were compared with those of microporous activated carbon fiber cloth (ACFC-20) and mesoporous tire-derived activated carbon (TDAC, surface area $\sim 690 \text{ m}^2/\text{g}$).

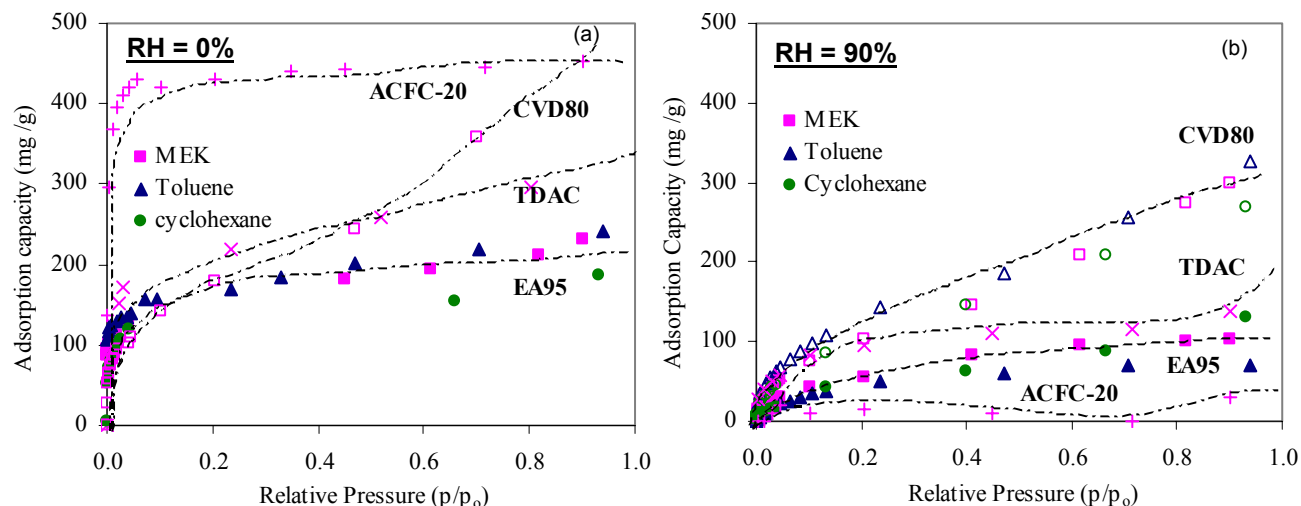


Fig. 4. Organic vapor adsorption isotherms on SWNTs and activated carbons at 25 °C and (a) 0% (b) 90% humidity conditions.

In dry conditions (RH = 0%), the adsorption capacities of SWNTs were much lower than those of ACFC-20 and were similar to those of TDAC. However, in humid conditions (RH = 90%) the adsorption capacities of SWNTs were higher than those of ACFC-20. In addition, in the presence of water vapor the organic vapor adsorption capacities of tested adsorbents were lower than those measured in dry conditions (Fig. 4).

The MEK adsorption capacities of samples EA95 and CVD80 and mesoporous TDAC in humid conditions were lower than in dry conditions. However, the total adsorption capacities (i.e., water + organic vapor) of these samples were comparable to their MEK adsorption capacities in dry conditions (Table 1). Similar results were also observed for the other VOCs tested. On the other hand, in humid conditions microporous ACFC-20 mainly adsorbed water vapor. Adsorption behavior of SWNTs for VOCs and water vapor were closer to those of a mesoporous carbon than the microporous carbon tested in this study.

Table 1. Maximum adsorption capacities (mg/g) of adsorbents at 25 °C.

SAMPLE	RH = 0%		RH = 90%	
	MEK	Water vapor	MEK	Total
EA95	232	105	97	202
CVD80	430	120	310	430
ACFC-20	584	650	15	665
TDAC	296	133	140	273

The adsorption isotherms were also analyzed to determine the possible sites for organic vapor adsorption in SWNTs. In dry conditions, organic vapor adsorption in SWNTs was observed at concentrations as low as $p/p_0 \sim 10^{-4}$. In humid conditions, however, both SWNT

samples did not adsorb organic vapors at concentrations below $p/p_0 \sim 10^{-2}$. This shows that in humid conditions most of the micropore volumes (which facilitates adsorption at low concentrations), i.e. the hollow internal space of SWNTs (i.e., site 1 and 2 in Fig. 1a), were saturated with water and VOCs adsorb mainly on the external surface (i.e., site 3 and 4 in Fig. 1a) of the bundles. Adsorption isotherms for samples EA95 and CVD80, Fig. 4b, represent adsorption on the peripheral surface of the bundles.

Conclusions

This study showed that the phenomenon of “aging” impacted N_2 adsorption properties and the nature of surface functionality of SWNT samples tested. “Aging” is most likely results from the chemical treatment employed for producing purified nanotubes. Organic vapor adsorption capacities of SWNTs were higher than those of microporous ACFC-20 when measured in humid conditions. Adsorption behavior of SWNTs for VOCs and water vapor were closer to those of a mesoporous carbon than the microporous carbon tested in this study.

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