Environmental Applications of Carbon Nanotubes on Quartz Filter

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ABSTRACT

Air pollution has become an important issue worldwide due to its adverse health effects. Among the different air contaminants, volatile organic compounds (VOCs) are liquids or solids with a high vapor pressure at room temperature that are extremely dangerous for human health. Removal of these compounds can be achieved using nano materials with tailored properties such as carbon nanotubes. Vertically-aligned multiwall carbon nanotubes (CNTs) were successfully grown on quartz filters by means of plasma enhanced chemical vapor deposition (PECVD). Furthermore, a plasma treatment was performed in order to modify the surface properties of the CNTs. The adsorption/desorption processes of three chlorinated compounds (trichloroethylene, 1, 2-dichlorobenzene and chloroform) on the CNTs were studied using mass spectrometry measurements with a residual gas analyzer.

KEYWORDS: *Volatile organic compounds, carbon nanotubes, adsorption, air pollution*

I. INTRODUCTION

A large number of households and industrials products contain volatile organic compounds (VOCs). VOCs can easily evaporate at room temperature and are extremely harmful for the health of human beings. Among various types of VOCs, chlorinated compounds are used frequently in a wide range of industrial products and chemical processes, polluting the environment and ground water resources. Therefore, it is desirable to control the chlorinated VOCs emission in air by utilizing various kinds of adsorption/removal processes. Carbon nanotubes (CNTs) are based in a unique material that possesses high mechanical strength, ballistic conduction, high temperature thermal stability and high surface area. All these extraordinary properties make them a useful material for various kinds of applications such as super capacitors, sensors, and field emitters and for the removal of contaminants from water and gases. Usually, carbon based adsorbents are used for the removal of contaminants due to their high surface area. The surface area of CNTs is in the range of 150-3000 m2/g, which is comparable to other carbon based adsorbents. CNTs have been shown to be an efficient adsorbent for the elimination of di benzo-p-dioxin from contaminant water. A number of features provide CNTs with superior adsorption properties than activated carbon; well defined structure, interstitial region between nanotubes in the bundles, grooves, curved surface outside of nano tube bundles, defect sites and, if the caps of nanotubes are open, the inner

surface of tube. Multilayer adsorption may also occur when organic chemicals are adsorbed on the surface of CNTs. In addition, it has been shown that CNTs display faster desorption for a wide range of non polar compounds. Generally, amorphous carbon and catalyst particles are also present on the surface of the as grown CNTs, which can significantly decrease the adsorption and desorption efficiency of the CNTs by blocking their pores. The removal of amorphous carbon is usually achieved by heating the CNTs at 300-500.C and the catalyst particles can be eliminated by acid treatment. This treatment results in the destruction of the structure and introduction of carboxylic groups in CNTs. Furthermore, it is rather difficult to control and very harsh for the graphitic walls of CNTs. Herein, the adsorption/desorption properties of chlorinated VOCs on quartz filter (QF), carbon nanotubes grown on QF (CNTsQF) and water plasma treated CNTsQF (wp- CNTsQF) have been investigated.

II. EXPERIMENTAL METHODOLOGY SYNTHESIS OF VAMWCNTS

VA-MWCNTs were grown on quartz filters by using radiofrequency plasma-enhanced chemical vapour deposition (rf-PECVD). A detailed description of the growth process and reactor used can be found elsewhere. A summary of the growth conditions is given in **Table 1**. Unlike our previous work, high-purity quartz (SiO_2) microfiber filters (Whatmantm) were used as substrates for the growth of CNTs. These quartz filters have 47 mm of diameter, 450 µm thickness and they are formed by long fibers having a diameter below 1.5 µm. Briefly, a thin layer of 3 nm Fe catalyst was deposited by rf-magnetron sputtering on a quartz filter and annealed at 680^0 C during 120 s (ramp time: 750 s) in hydrogen atmosphere to obtain Fe nano islands. Then, the precursor gas (NH3, 100 sccm) and the carbon source (C2H2, 50 sccm) are allowed to enter the reaction chamber and the PECVD reaction takes place with the formation of CNTs at a constant pressure of 100 Pa.

Table 1. Summary of the VA-MWCNTs growth conditions.

Parameter	Value
Catalyst layer thickness	3 nm
Annealing time	870s
PECVD process temperature	700ºC, 730ºC
PECVD process plasma power	50 W
PECVD process time	900s, 1800s

In a further step some of the samples were treated with water plasma to remove amorphous carbon and introduce oxygen groups on the CNTs surface. The CNTs were treated with 10 W rf power and 135 Pa water pressure for 120 s, which is only specific to the removal of amorphous carbon and the introduction of different oxygen containing functional groups, without destroying the nanotubes. The adsorption/desorption properties of CNTs were studied using three chlorinated VOCs; trichloroethylene, chloroform and 1, 2-dichlorobenzene. The chemicals were from high purity (99.9%, Sigma-Aldrich) and were used undiluted.

III. STUDIES ON ADSORPTION

A system was devised to study the adsorption of volatile organic compounds by CNTs-based filters (see **Figure 1**). The system has three channels made of a stainless steel tube with an internal diameter of 4 mm and an external diameter of 6.32 mm. A flask containing the chlorinated compound to be studied is placed at the start of the central channel, and is connected to a three-way valve. Both left and right channels have a filter holder at the end, where the carbon nanotubes filter is placed. The whole system is connected to a turbo molecular pump, which allows operation under high vacuum conditions (10-5 Pa) and all experiments were carried out at room temperature. A filter without carbon nanotubes is placed in the right channel and is taken as a reference. In the left channel different types of carbon nano tube filters are placed and systematically analyzed (untreated CNTs and wp-treated CNTs). In order to perform the measurements, a lab view program controls the opening of the pneumatic valves present at the entrance of each channel during a period of 50 ms, letting the chlorinated compound flow through the filter under study.
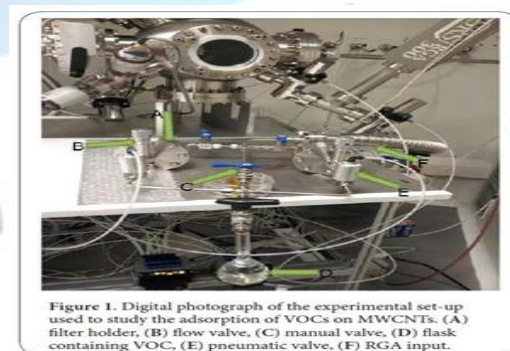

Figure 1. Digital photograph of the experimental set-up used to study the adsorption of VOCs on MWCNTs. (A) filter holder, (B) flow valve, (C) manual valve, (D) flask containing VOC, (E) pneumatic valve, (F) RGA input.

Immediately after opening the valves, the RGA detects a fast increase of the partial pressures of the species followed by a slower decrease related to adsorption and desorption processes. The partial pressure of the compounds can be related to the

concentration of the chemical species in the gas phase. Therefore, we can get an idea about the kinetics of the adsorption/desorption processes that occur at the surface of the different CNTs-based filters by representing the partial pressure versus time in a semi-logarithmic scale. Since the adsorption process was too fast to be analyzed with our setup, we studied the desorption curves of the different compounds. The measurements could be fitted with a double exponential equation (1), which indicates the presence of two desorption processes. Depending on the interactions between VOC and filter, only one of the two mechanisms was observed. In those cases, a simple exponential equation was used.

$$P(t) = P_R + P_1 \exp\left[-(t - t_0)/\tau_1\right] + P_0 \exp\left[-(t - \tau_0)/\tau_2\right] \quad (1)$$

Where *P1* and *P2* are partial pressures in Pa, *PR* is the residual pressure in Pa, *t* is the time in s, *t0* the initial time of desorption process in s, τ*1* and τ*2* are the characteristic times in s.

IV. CHARACTERIZATION TECHNIQUES

Field emission scanning electron microscopy (FESEM) (Hitachi S-4100, Japan) and high resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100, Japan) were used for the morphological and structural characterization of CNTs. RAMAN spectroscopy was performed to evaluate the quality of the CNTs using a micro-Raman system (Horiba LabRam HR800, Japan). A green laser of wavelength 532 nm, 0.25 mW power and a 100X objective were used during the measurements. Quadruple mass spectroscopy-residual gas analyzer (SRS QMS-RGA-300, USA) was used to analyze the partial pressure of the chemical species that passed through the filter.

V. RESULTS AND DISCUSSION

A. Morphological characterization

In order to increase the VOCs adsorption capacity of the quartz filters, a large surface area is needed, which can be achieved by growing long CNTs on top of them with a high surface density. Based on our experience in growing CNTs on c-Si wafer, growth conditions were chosen close to the optimum ones previously obtained [**7**]. Here, the substrate is a SiO2 filter with the same chemical composition as the native SiO2 present on a silicon wafer. Thus, we expect that similar conditions will provide the growth of CNTs on quartz filters. However, in the present work, the surface is not flat, but rather a 3D matrix of quartz microfibers, which can affect

the nucleation of catalyst particles and as a consequence the CNTs structure and morphology.
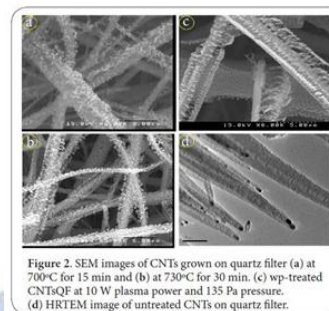

Figure 2. SEM images of CNTs grown on quartz filter (a) at 700ºC for 15 min and (b) at 730ºC for 30 min. (c) wp-treated CNTsQF at 10 W plasma power and 135 Pa pressure. (d) HRTEM image of untreated CNTs on quartz filter.

(Figure 2a) shows CNTs grown on QF at an annealing temperature of 680.C, a growth temperature of 700.C and growth time of 15 min. Under these conditions the CNTs were not vertically aligned and their density was also not very high. (Figure 2b) shows a SEM image of CNTs grown at a higher growth temperature (730.C) and longer deposition time (30 min). The density of CNTs increases significantly with respect to those grown at 700.C and they are vertically aligned in all directions of the quartz fibers. Therefore, these conditions are more suitable for the growth of CNTs on quartz filters and with a high surface area. (Figure 2c) shows wp-treated CNTsQF at an rf power of 10 W and 135 Pa water pressure. Most of the amorphous carbon is removed while keeping the alignment and a difference in texture can be appreciated in comparison to untreated CNTs. TEM analysis of untreated MWCNTs clearly show their "bamboo"-like structure, as well as the amorphous carbon on the surface and Fe catalyst particles on the tips of CNTs (Figure 2d).

B. Raman spectroscopy

Analysis of MWCNTs Raman spectra is usually performed by interpreting the relation between two well-known bands; D and G, located at ~1350 cm-1 and ~1580 cm-1, respectively. D band is a double resonance mode and its appearance is due to the existence of amorphous carbon, structural disorder and defects caused by pentagons or heptagons on the nanotubes. G band is the tangential stretching mode of sp2 bonded carbon atoms in graphene-like structures. Analysis of the ratio between the D and G band intensities (ID/IG) gives us information about structural disorder. (**Figure 3**) shows Raman spectra of CNTsQF and wp- CNTsQF. The fitting process was improved by the introduction of two additional bands; I band at ~1210 cm-1 and D// band at the frequency of ~1520 cm-1. D band position was 1360 cm-1 with full width half maximum (FWHM) of 83 cm-1 for

untreated CNTsQF. After the water plasma treatment a very small shift in the D band position and FWHM of wp-CNTsQF was observed, because the treatment is mainly specific to the removal of amorphous carbon, i.e., very little etching of CNTs walls, and to the introduction of functional groups in CNTs. The ID/ IG ratio was 1.1 for untreated CNTsQF and increases up to 1.3 for water plasma treated CNTsQF, which suggests a higher disorder in the structure of treated CNTs. After the water plasma treatment I and D// bands become more prominent. The enlargement of the D//band is in agreement with the expected attachment of polar groups on the CNTs surfaces. The area of the D//peak increases from 170 to 547 and the ID///IG ratio from 0.46 to 0.62, for untreated CNTsQF and wp-CNTsQF, respectively.

C. STUDY ON ADSORPTION

CNTs are normally grown in the form of bundles and behave as heterogeneous sorbents. They provide four sites for the adsorption of contaminants, namely; interstitial channels, external groove sites between the bundles, external surfaces and, if the tips are open, i.e., without catalyst particles that remain on the top of each individual nano tube, internal surfaces of CNTs. Since the presence of amorphous carbon reduces the adsorption/desorption efficiency of CNTs, it is desirable to remove it while preserving the structure of the CNTs. Here, a water plasma treatment was used to eliminate amorphous carbon. In addition, the treatment introduces oxygen functional groups and defect sites on the CNTs surface that can significantly enhance the adsorption efficiency of contaminants. The three chlorinated compounds are non-polar solvents with a low solubility in water. In particular, the water solubility values are 0.11, 0.815 and 1.4%, which follow the same trend as the molecular dipole moment; 0.8, 1.01 and 2.5 D for trichloroethylene, chloroform and 1, 2-dichlorobenzene, respectively. For all the studied VOCs characteristic desorption times increased from bare QF to CNTsQF and wp-CNTsQF. The latter being the one with the longest characteristic desorption 0020 times (see Table 2).

Table 2. Characteristic desorption times of different VOCs on quartz filter, CNTsQF and plasma treated CNTsQF.

VOC	Filter $\tau_1(s)/\tau_2(s)$		
	QF	CNTsQF	wp-CNTsQF
trichloroethylene	0.85/1.74	-/2.38	-/2.70
chloroform	0.65/2.28	0.99/2.32	1.28/2.70
1,2-dichlorobenzene	1.10/-	3.25/13.76	-/15.29*

Due to the small number of points, this value has a large error associated with it. However, the value fits well with the one obtained for desorption of 1,2-dichlorobenzene on CNTsQF, and therefore, it is regarded as reliable. In the case of trichloroethylene it was found that carbon nanotubes increase the time constant of the slow desorption mechanism (τ_2) (Table 2, Figure 4a), which is assumed to be mainly related to π-π interactions between CNTs and the C=C bond present in C2HCl3 [14,17]. Due to the removal of amorphous carbon after the water plasma treatment, and the corresponding surface area enhancement that provides more space for solute adsorption, the desorption time of the wp- CNTsQF sample increased with respect to that of untreated CNTs (Figure 4a, Table 2). Moreover, the introduction of oxygen groups on the CNTs surface enhanced the π-EDA interactions with the VOC.
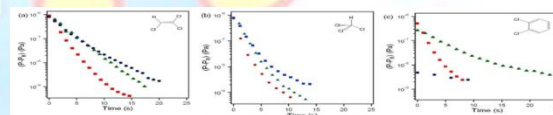
Figure 4 Comparative desorption study. Desorption process of (a) trichloroethylene, (b) chloroform and (c) 1, 2- dichlorobenzene.

Owing to the lack of π-electrons in chloroform, the main interactions with CNTs are π-EDA and hydrogen bonding. The water solubility and dipole moment are slightly higher than for trichloroethylene and hence, the interactions are stronger and characteristic times longer (Table 2, Figure 4b). However, the total desorption time is shorter than for trichloroethylene, probably due to steric effects that avoid the adsorption of more molecules. In comparison to the other studied VOCs, 1, 2- dichlorobenzene contains an aromatic ring and combines a high polarity index with a high solubility in water. Thus, the main interactions with CNTs are supposed to be polar-π interaction, π-stacking and hydrogen bonding. Plasma- treated CNTs without amorphous carbon and with oxygen functional groups attached on their surface increase the aromatic-aromatic interactions between 1,2-dichlorobenzene and aromatic rings

present in the CNTs structure. Due to the large difference in the characteristic time between bare QF and carbon nanotubes-based filters, we can assume that possibly a multilayer condensation occurs (π-stacking interactions), which significantly increases their adsorption (Figure 4c). From the above results it was not possible to determine the difference between the mechanisms that govern the two characteristic desorption times (τ1 and τ2). Future experiments should be carried out in order to explain the observed behavior.

VI. CONCLUSIONS

Vertically-aligned multiwall carbon nanotubes have been successfully deposited on quartz fiber filters for environmental applications. A water plasma treatment of the grown nanotubes introduces oxygen functional groups on their surface without modification of their alignment. The presence of inner cavities and functional groups on the CNTs surface contribute to improve their capability to remove or selectively detect organic pollutants. It has been proven that the adsorption/desorption capacity of chlorinated VOCs by CNTsQF and wp-CNTsQF is higher than that of bare QFs. In addition, the presented results show that CNTsQF and wp-CNTsQF affinity for the adsorption/desorption of chlorinated VOCs increases with compound solubility in water and polarity. Finally, molecules with aromatic rings present stronger interactions with CNTs (π-stacking) and thus, significantly longer desorption times and time constants.

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