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Preconcentration of Volatile Organics on Self-Assembled, Carbon Nanotubes in a Microtrap

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This paper reports the self-assembly of carbon nanotubes (CNTs) on the inside wall of a steel capillary to fabricate a microtrap for the adsorption/desorption of trace organics. The microtrap functioned as a nanoconcentrator and an injector for gas chromatography (GC). The CNTs were deposited as a thin film by catalytic chemical vapor deposition from either CO or C₂H₄ as the precursor. The sorbent film synthesized from C₂H₄-CVD (CVD = chemical vapor deposition) had higher CNT density and thus was a stronger sorbent. In general, the CNT microtraps showed high-capacity adsorption and fast quantitative desorption, and the process showed excellent precision. This study demonstrates that CNT films can be deposited quite easily in a steel capillary for use in different analytical applications, and CNT films can perform as efficiently as packed-bed carbon sorbents.

A single-wall carbon nanotube (SWNT) is a hexagonal layer of carbon atoms (a graphene sheet) that has been rolled up to form a seamless cylinder. A stack of these sheets also rolls up into concentric cylinders to form a multiple-wall carbon nanotube (MWNT). These types of nanoscale (5–100 nm o.d.) carbon filaments were first prepared in the 1970s; however, systematic studies of this material did not begin until the observation of MWNTs in the early 1990s.¹ Since that time, carbon nanotubes (CNTs) have been the subject of intense research because of their novel physical, chemical, and electrical properties.^{2,3} CNTs are expected to play important roles in future sensing and separations techniques because they represent a novel class of material with varied functionality to facilitate adsorption. The internal pores of the CNTs are large enough to allow small molecules to penetrate. Large sorption surfaces are also available on the outside and in the interstitial spaces within the nanotube bundles that are held together by van der Waals forces. The possibility of chemical functionalization of the CNT side walls also opens additional possibilities for sorption of different molecules.

On the basis of current developments, techniques for CNT synthesis may be classified under three major categories, namely, laser ablation,⁴ catalytic arc discharge,⁵ and chemical vapor deposition (CVD).^{6–8} While the first two methods are excellent

for large-scale production, they cannot be used for self-assembly on different substrates. Catalytic CVD appears to be the method of choice for direct deposition on a device or a structure. Several variations of this technique have been reported in the literature.^{9–11} High-purity SWNTs have been grown by the catalytic decomposition of methane,¹² by the catalytic disproportionation of carbon monoxide (CO) under high pressures (the so-called high-pressure carbon monoxide (HIPCO) process),¹³ and at atmospheric pressures.^{14–17} Cheng et al.¹⁸ produced CNTs at 1200 °C in a heated flow of benzene together with ferrocene and thiophene precursors to form floating catalytic particles, whereas Maruyama et al.^{19,20} generated CNTs at temperatures down to 550 °C using ethanol under low-pressure conditions. Low-pressure CVD using ethylene and propylene was employed by Sharma and Iqbal²¹ to observe in real time the in situ growth of SWNTs and MWNTs in an environmental transmission electron microscope.

Adsorption of gases on CNTs have been studied quite extensively, both by theoretical means and by temperature programmed desorption techniques.^{22–25} For example, H₂ storage

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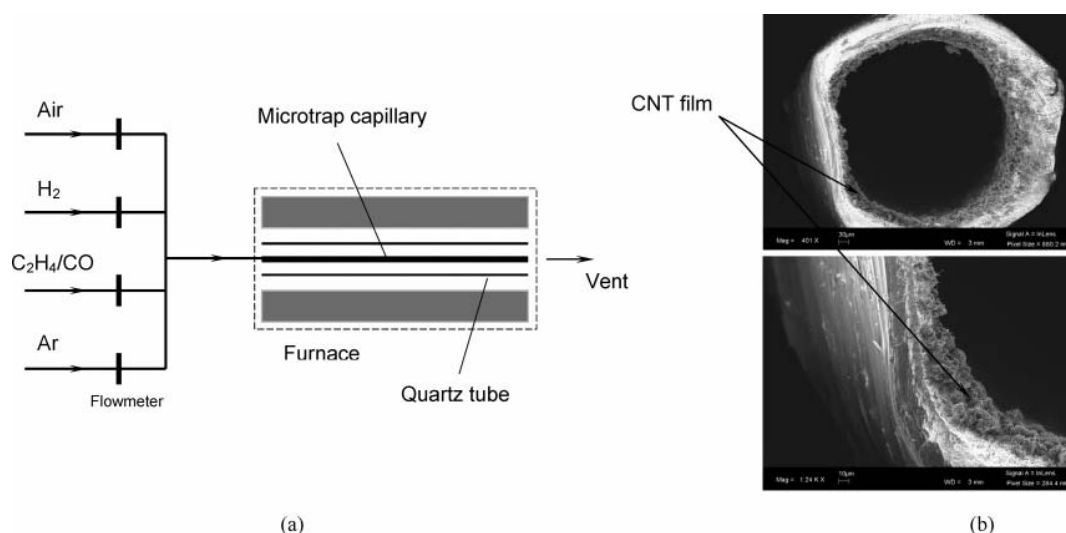


Figure 1. (a) Schematic diagram of the CVD setup. (b) Cross-sections of a CNT microtrap grown in steel capillary by CO-CVD.

has been mainly attributed to physisorption, both inside the tube and in the interstitial region between tubes in a bundle.²⁶ The adsorption of organics on CNTs has also been studied^{27,28} and is found to be somewhat different. For example, chemisorption was suggested as the mechanism for the adsorption of acetone²⁸ on CNTs using sonication. This conclusion was based on the high activation energies of desorption, which were significantly higher than those from graphite (known to show physisorption) and the latent heat of vaporization of liquid acetone. Moreover, the activation energies of desorption were comparable to those of covalent bond energies.

CNTs can be synthesized in different forms (SWNTs and MWNTs), in different sizes, and with different functionalities, because of which they may have different affinity and selectivity for a wide range of analytes. It is therefore conceivable that CNTs will emerge as high-performance, high-temperature sorbents for analytical applications. Two aspects of CNTs are important for analyte retention, namely, adsorption and desorption. The physical/chemical affinity between the sorbate and the sorbent needs to be optimum for these to occur.²⁹

Here we report the application of self-assembled CNTs in the nanoscale adsorption/desorption of small organic molecules. The selected application device is a microtrap that can be used in chemical sensing, trace monitoring, and gas chromatography (GC). The CNTs are self-assembled as a thin film on the inside walls of the steel capillary. Trace (parts per million, ppm) levels of organics are then allowed to be adsorbed and concentrated on the CNTs and then desorbed for detection.

EXPERIMENTAL SECTION

CVD System and Conditions. The self-assembly of CNTs in 250 and 500 μm i.d. capillaries was carried out in a tube furnace

by the CVD method described previously²¹ and modified for direct growth inside the steel capillaries. This is shown in Figure 1. Both CO and C₂H₄ were used as the carbon source for the CNTs. Two types of microcapillaries were tried here; one was silica-lined stainless steel, and the other was untreated stainless steel. Nanocrystals of iron are well-known to catalyze the growth of CNTs,³⁰ so the nanostructured regions of the polycrystalline iron tube provides the catalytic surface for CVD growth and assembly of the nanotubes. In the case of silica-coated steel, sparse growth appeared without the catalyst, because fine-scale porosity in the silica coating probably provided exposed iron for catalytic growth of CNTs. CNT growth in steel tubing was carried out as follows. First the capillary was heat-treated in air at 500 °C for 30 min to oxidize the surface, and then the surface was reduced in a flow of H₂ at 500 °C for 30 min. The oxidation–reduction led to the formation of nanostructured catalyst³¹ on the tube surface. After this, CVD was carried out in a flow of CO or C₂H₄ at 700 °C for between 1 and 3 h. All flow rates were kept at 10 mL/min. This process formed the microtrap with a thin film of CNTs. The microtrap was then heated in a stream of oxygen for 5 h at 300 °C to oxidize any amorphous carbon and carbonaceous materials formed during the growth process.³¹

Previous adsorption studies with organics have been carried out by mixing a gas or a liquid solute with the CNTs and then desorbing the solutes.²⁷ Trapping of low-concentration organics from the gas phase is quite different than those from liquid phase.³² In this study, the adsorption took place from a gaseous stream containing trace levels of organics. The ppm level organic stream containing toluene and hexane was generated by diffusing a controlled amount of the analytes from the diffusion capillary into a flow of N₂. This technique is well-known and has been described elsewhere.³³ The stream flowed constantly through the microtrap, and the organics were trapped in the self-assembled CNT film. An electrical pulse was applied to the metal capillary at predetermined intervals (every few minutes) to desorb the

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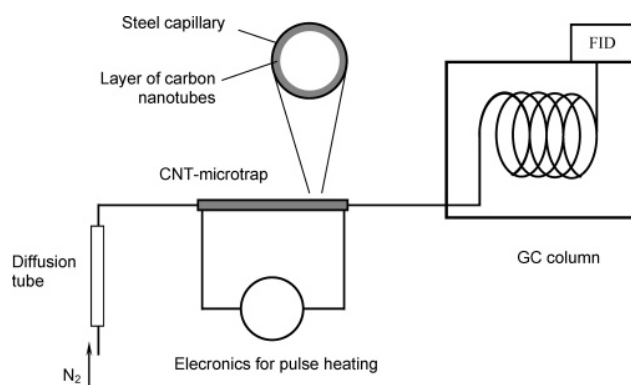


Figure 2. Schematic diagram of the experimental setup.

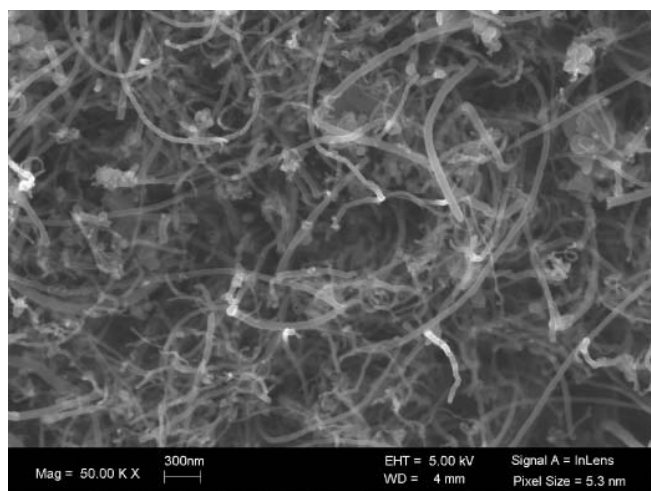
trapped organics. Duration of the pulse was between 1 and 1.5 s, which raised the microtrap temperature to 300–400 °C.³⁴ Rapid heating caused the vapors from the “desorption pulse” to be injected into the detector. A microprocessor-based controller was used to control the interval and duration of the electrical pulses. This technique has been described in detail elsewhere.^{34–36}

Analytical System. In general, the microtrap can be used with any sensor or detector. Here it was tested with a conventional flame ionization detector (FID). The analytical system used is shown in Figure 2. A gas chromatograph (Hewlett-Packard 5890) equipped with an FID was used for analysis. A 0.53 mm i.d., 30 m capillary column (DB-624, J&W Scientific) was used. Gases such as air, nitrogen, and hydrogen were purchased from Matheson Co., NJ. Nitrogen was used as a carrier gas with a flow rate of 7 mL/min.

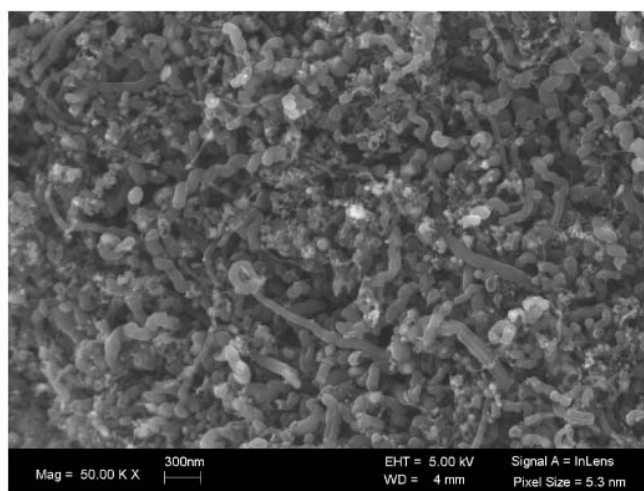
Both silica-lined and plain stainless steel tubings were used to fabricate microtraps. They were of 30 cm length and 0.53 mm i.d. CO and ethylene were used to self-assemble the CNT layer as the active surface.

RESULTS AND DISCUSSION

Typical structures of CNTs in the films inside the capillaries are shown in Figure 3a,b. In the case of silica-coated steel, only sparse growth of CNTs was observed without the catalyst. Consequently, the silica–CNT film showed poor sorption capacity.



a)



b)

Figure 3. CNT structure in the microtrap (a) by 1 h C₂H₄–CVD and (b) by 1 h CO–CVD.

So, uncoated stainless steel capillaries were used for further experiments and represent the data presented here. CNTs from CO were relatively short, and the diameters ranged from 13 to 100 nm, whereas much longer tubes with diameters ranging from 25 to 70 nm were formed using C₂H₄. The CNTs deposited were radially aligned inside the tube. Noodlelike structures crisscrossing in different directions and a large number of twisted tubes were also formed. Previous studies have reported similar formation of nanotubes that were aligned either perpendicularly or horizontally to the substrate, particularly under plasma conditions.²⁰ The thickness of the CNT films grown in the microcapillary could be increased by increasing the CVD deposition time. Films as thick as 30 μm were formed. The thickness is an important parameter because it determines the sorption capacity and mass transfer in the CNT film. Raman spectra taken from the inside surface of the cut capillary did not show the characteristic peaks associated with the strongly diameter dependent radial breathing mode of SWNTs below 300 cm^{−1}, which suggested that SWNTs were not formed under the used conditions.

The gas sample stream containing organics passed the microtrap placed on-line and then was directed to the detector. The organics were alternately adsorbed and then desorbed from the CNT film by electrical heating. The electrical pulses (injections) were made at fixed intervals of time, and corresponding sequences of signal pulses were observed at the detector. This is shown in Figure 4a. Reproducibility was excellent, and injection pulses could be continued. The coefficient of variation of detector signal was 1.02%. This demonstrated that both the adsorption and desorption from the CNT film was reproducible over long periods of time.

As mentioned before, the two desirable features for sorbate trapping in analytical applications are the strong sorption and fast desorption. These often tend to be mutually exclusive, because conditions of strong sorption do not lead to fast desorption. Thus, both adsorption and desorption processes are important in the CNT–microtrap operation. Fast desorption leads to narrow injection bands. The peak width at half-height was around 1.4 s, which is compatible with high-resolution GC, and proved that the

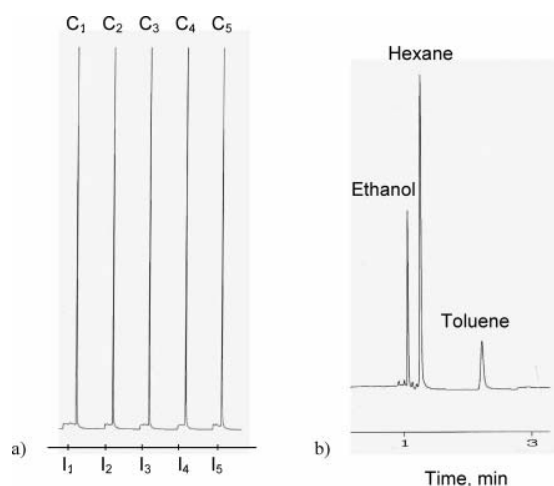


Figure 4. (a) Sequence of desorption peaks generated using the CNT microtrap with ppm level toluene as the sample. Injections were made at I_1 , I_2 , ... (every 2 min), resulting in a sequence of concentration pulses C_1 , C_2 , (b) Typical chromatogram generated using the CNT microtrap as an injector for GC separation.

desorption from the CNT film was rapid. This was possible despite the strong chemisorption of organics suggested previously.³¹ Analytical applications require the elimination of any residual or memory effects; here the desorption was found to be completely reversible. The rate of desorption depends on the maximum temperature reached and the heating rate. Because the heat must be transferred from the tube wall through the CNT film, the heat transfer is also an issue. Based on previous observations where microtraps of the same dimensions were resistively heated under similar conditions,³⁶ the estimated heating-cooling cycle is of the order of seconds and the typical microtrap temperature is between 350 and 400 °C. This suggests that these conditions were appropriate for adsorption-desorption from the CNT film as well.

The fast desorption from the CNT film allowed the microtrap to be used as an injector for gas chromatography. Figure 4b shows a chromatogram generated by alternate trapping and desorption of several small-molecule organics. The high-resolution separation is also attributed to the fast desorption from the CNT film.

The sorption capacity of the CNT film in the microtrap was evaluated by studying the breakthrough point of the microtrap, which is defined as the time required by an analyte to elute through the trap, i.e., the time for which the organic molecules are retained^{37,38} in the CNT film. This is known to be a function of the capacity factor, length, and flow rate.³⁷ It has been reported that the breakthrough time can be accurately determined by operating the microtrap at varied injection intervals.^{36,38} As the interval increased, the amount of organics accumulated increased. However, this did not continue indefinitely, as the sample began to breakthrough, and the response did not increase any further. The leveling off point has been referred to as the breakthrough time.³⁸ Figure 5 shows the breakthrough of hexane and toluene on the microtrap. The response profile showed a linear increase

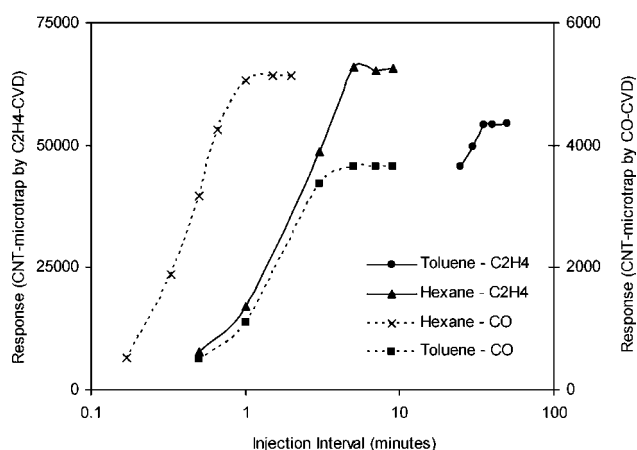


Figure 5. Detector response as a function of injection interval using a CNT microtrap made by CO and C₂H₄-CVD. The flow rate was 7 mL/min. The dotted line represents data by CO-CVD, and the bold line, by C₂H₄-CVD.

with the injection interval up to some point, beyond which the response remained constant. Under similar process conditions of flow rate, pressure, and CVD deposition time, CO formed a lower capacity film (i.e., lower breakthrough time) compared to that from C₂H₄. This is attributed to the higher densities of CNTs formed when C₂H₄ was used as the precursor. Consequently, the breakthrough times were 4.5 and 12 times larger for hexane and toluene when the microtrap was fabricated via C₂H₄-CVD. The relatively higher retention of toluene as compared to the aliphatic hydrocarbon is also interesting. While a larger retention is expected on the basis of lower volatility of toluene, the unusually large difference (4.5 min versus 35 min) is attributed to the strong π - π interactions between the aromatic toluene and the graphitic ring structure of the CNTs. On the basis of comparison with previously published data,³⁶⁻³⁸ the trapping capacity of a micrometer-scale CNT film appears to be higher than that of a packed bed of commercial activated carbon (Carbotrap, Supelco Inc., Supelco Park, PA). Consequently, this opens the doors to the application of high-capacity, carbon-based CNT films as an alternative to packed sorbent beds.

CONCLUSION

The self-assembled multiwall CNTs were formed by CVD on the inside wall of stainless steel capillaries, with the iron in the steel serving as the catalyst for nanotube growth. This relatively simple approach can be applied to CNT-based analytical devices, where the CNT film provides an active surface for adsorption/desorption of organic molecules. The CNT film in the capillary showed high adsorption as well as fast desorption of small organic molecules, such as hexane and toluene. The film made by C₂H₄-CVD showed higher CNT density, and thus higher sorption capacity. The sorption of toluene was much stronger than hexane, which is attributed to the π - π interaction between the CNT side wall and the aromatic ring of toluene. Fast desorption (measured as 1.4 s bandwidth at half-height) is an important feature for adsorption and sensing applications.

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