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Self-Assembly of Carbon Nanotubes via Ethanol Chemical Vapor Deposition for the Synthesis of Gas Chromatography Columns

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The synthesis of the gas chromatography stationary phase by molecular self-assembly of carbon nanotubes (CNTs) via a novel ethanol chemical vapor deposition process is presented. A major advantage is that ethanol was found to be an excellent carbon source that generated highly pure multiwalled carbon nanotubes with very little non-tubular carbon impurities. The nanotubes were not vertically aligned but lay flat out on the column surface in a randomly distributed configuration. The CNT phase was able to separate a wide range of organic compounds with diverse polarity and volatility, where the number of plates per meter ranged from 900 to 1280. It also showed classical chromatographic behavior and good precision.

Due to their unique physical, chemical, and electronic properties, carbon nanotubes (CNTs) have found diverse applications ranging from molecular electronics to drug delivery.^{1,2} Their unique sorption properties have also received special attention in applications such as gas storage and environmental sorbents.^{3–6} A wide range of surface areas (110–407 m²/g) have been reported for CNTs,^{7–10} and they have been incorporated in analytical techniques such as chromatography, SPE, SPME, μ -SPE, and membrane extractions.^{11–14}

The conventional approach to improving mass transfer in gas–solid chromatography (GSC) separation is to reduce the

particle size. Typical stationary phases used in gas–solid chromatography use porous materials, where diffusional mass transfer plays an important role, and their microporosity leads to large surface areas for enhanced sorption capacity.^{15,16} CNTs are an attractive alternative to conventional GSC stationary phases because their large aspect ratio provides high external surface area, and their nonporous nature leads to fast mass transport.^{17,18} The CNTs have been used as GC stationary phases in the packed and self-assembled formats, and a combination of CNTs and silica microspheres have been used as stationary phases for LC.^{19,20} A wide range of compounds from small gas molecules to relatively large polycyclic aromatics^{21–25} have been separated on CNT-based gas–solid chromatography columns.

In general, CNTs are implemented in different devices as particles, thin films, polymer composites, and self-assembled layers. Molecular self-assembly is an attractive bottom up approach to synthesize supramolecular architectures. Synthetic methods for controlled morphology, orientation, and surface designs^{26–28} remain a challenge. The combination of good self-assembly and superior sorbent properties can lead to the development of novel stationary phases for open tubular GC columns. Our previous efforts at making GC columns involved chemical vapor deposition (CVD) using small molecules such as methane, ethylene, and carbon monoxide as the precursors.^{21,22} Here the surface was prepared to be catalytically active, and the vertical growth of CNTs, predominantly multiwalled nanotubes (MWNTs), took place on the surface.

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Purity of the CNT phase is an important consideration because the CNT growth occurs along with amorphous and other nontubular carbon (NTC) impurities. NTC tends to be disordered, be porous, and introduce diffusional resistance that is detrimental to rapid mass transfer.^{7,29} Extensive oxidative cleanup procedures that may also lead to CNT damage are necessary to eliminate NTC.^{30–32} Typically, the hydrocarbon precursors tend to generate a significant amount of NTC,^{33,34} while oxygen-containing sources such as ethanol are known to produce significantly cleaner CNTs.^{35,36} This is because ethanol is known to generate OH radicals that oxidize amorphous carbon.^{37,38} We have also reported the synthesis of single-walled nanotubes (SWNTs) on silica-lined surfaces using an external catalyst precursor (such as CoNO_3) dissolved in ethanol for open tubular columns. This was introduced under a flow of hydrogen to reduce the metal salt at high temperature to generate Co nanoparticles to serve as catalysts.²³ This is a relatively complicated process.

The objective of this research was to explore one-step approaches to the self-assembling of relatively pure CNTs on stainless steel columns via ethanol CVD for open tubular GC columns.

EXPERIMENTAL SECTION

All chemicals were of analytical grade and purchased from Sigma Aldrich, Inc. (St. Louis, MO, USA) and were used without further purification. All gases were zero grade and obtained from Matheson Tri-Gas (Montgomeryville, PA). Two substrates, namely, 304 SS (Alltech, Deerfield, IL) and silica-lined, Silicosteel metal capillary tubings (Restek, Bellefonte, PA), were tested for the self-assembly of CNTs. Initial testing showed that the latter did not generate enough CNTs, and they were not tested further.

Prior to CVD, the tubes were washed with acetone to remove any particles/impurities. The tubes were 1–2 m long, with 0.53 mm i.d. The CVD system previously reported was used for the fabrication of GC columns and is shown in Figure 1.^{21–23,30} The major alteration to this system was the use of ethanol as a carbon source. The ethanol was aspirated into the steel tube as shown in Figure 1. Steel tubings were coiled and placed inside the furnace tube. Then Ar was introduced, and the furnace was allowed to heat to 550 °C. At this temperature the Ar was shut down, and air flow was initiated at a flow rate of 10 mL min⁻¹ for a period of 30 min. The objective here was to generate iron oxide on the surface to act as the catalyst for CNT growth. Then the air flow was stopped, and the furnace was allowed to heat to 700 °C under the argon flow rate of 10 mL min⁻¹. At that point,

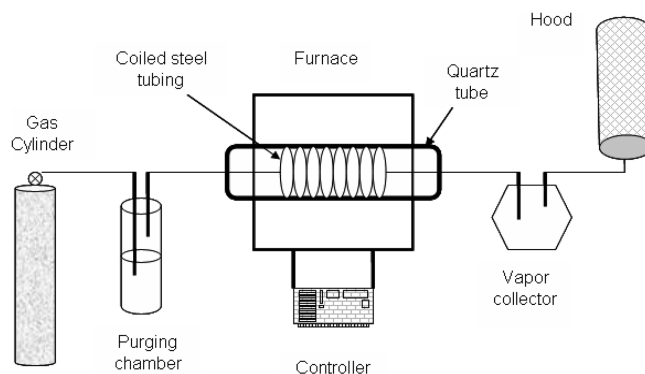


Figure 1. Schematic diagram of the CVD system.

ethanol was aspirated using Ar, and typical CVD time was between 15 and 60 min. Check valves (R. S. Crum & Co., Mountainside, NJ) were placed on both lines to restrict backflow. Taking into account that ethanol was being used at high temperature, the experiments were carried out in a fume hood, and necessary safety precautions were taken. Prior to their use in gas chromatography, the columns were treated at 200 °C in air for 1 h to oxidize amorphous carbon and other impurities generated during the process. Later, the column was heated in argon at 425 °C for 1 h to anneal and remove any low-boiling impurities.

To study the CNT coating, 1-cm-long segments were cut from the steel tube at different equidistant locations and were analyzed using a Leo 1530 VP (Carl Zeiss SMT AG Company, Oberkochen, Germany) field emission scanning electron microscope. The SEM images provided insight into the distribution, morphology, and arrangement of the CNT coatings inside the GC column.

Gas Chromatography. A gas chromatograph (model Varian 3400, Varian, Inc., Palo Alto, CA, USA) equipped with a conventional flame ionization (FID) was used in this study. A Perkin-Elmer Laboratory Computing Integrator model LCI-100 (Waltham, MA, USA) was used for data acquisition. Injections were made using a 10 μL Hamilton model 701 μL syringe (Hamilton Co., Reno, NV) through a split–splitless injection port. Injector and detector temperatures were set at 250 °C, and a typical injection volume was 1.0 μL unless otherwise specified. All injections were performed in the split mode with the split ratios varying between 1 and 20. N_2 was used as a carrier gas with a flow rate of 3 mL min⁻¹. The FID gases were comprised of air flow at 300 mL min⁻¹ and hydrogen at 30 mL min⁻¹. All GC measurements were repeated at least three times.

RESULTS AND DISCUSSION

CNTs growth are promoted catalytically.^{21–23,30} In the absence of an external catalyst, the silica-lined tube showed sparse growth of CNTs and was not studied further. The stainless steel tube surface was made catalytically active by oxidation in the presence of air to the respective metal oxides, which proved to be an effective catalyst. SEM images of steel tubing surface before and after heating in air at high temperature are shown in Figure 2(a, b), respectively. The CNT coatings were assessed at equidistant spots along the column. It appeared to be consistent, and no bare spots were observed. Figure 2 c, d) shows SEM images at both ends of the column. Multiple GC columns were analyzed to check reproducibility, and they showed similar results. It is evident that

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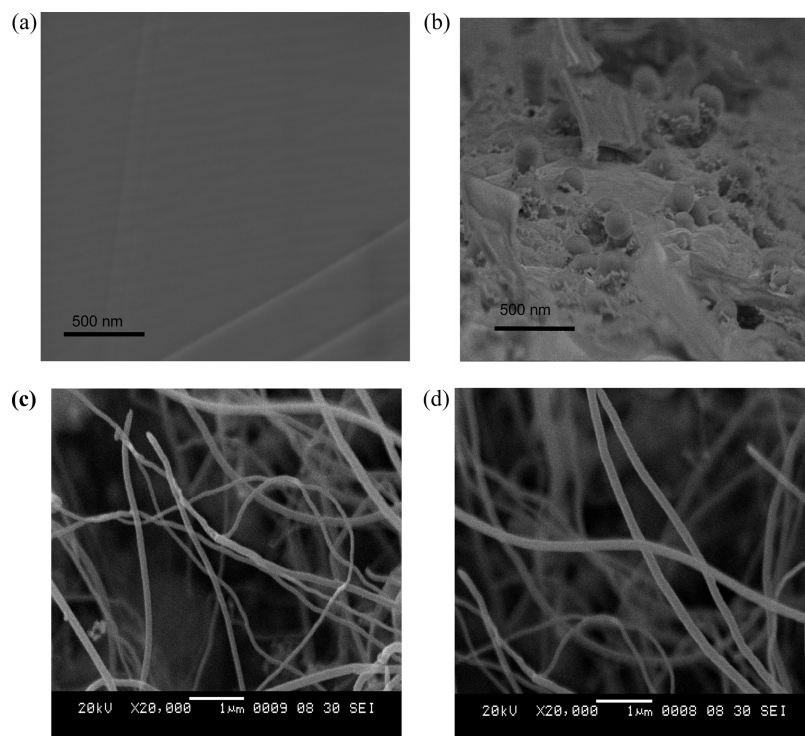


Figure 2. SEM images of (a) bare steel tubing surface (b) surface after preparation in air at high temperature. (c) CNT coating at the start of the column. (d) CNT coating at the end of the column.

the ethanol was a good carbon source and could produce highly pure CNTs with very little amorphous carbon. This was a major advantage of this process compared to ethylene CVD reported before.^{21,22} The CNT distribution was quite different from those reported previously.^{21–23,30} The CNTs were not vertically aligned but lay flat out on the tube surface in random noodle-like configuration. They were morphologically different from the CNT films reported before.^{21,23,30} Therefore, changing the carbon source led to the formation of CNTs with different characteristics and spatial distribution,^{21,23} and it is expected that these would effect the retention behavior differently for different types of molecules. The nanotubes appeared to be closed ended, therefore the outer walls of CNTs were expected to be the main contributor to analyte retention.

The separation efficiency of the CNT column was evaluated with diverse organic compounds. The boiling point of these analytes ranged from 64.7 to 217 °C (Table 1). Figure 3(a, b) shows baseline separation of straight chain and aromatic compounds, where resolution varied between 1.7 and 1.8. These compounds eluted in the order of increasing boiling points. Several compounds were tested, and the chromatographic parameters are as listed in Table 1. These were obtained under isothermal conditions and at an optimum flow rate of 3 mL min⁻¹. The number of theoretical plates (*N*) per meter varied between 900 and 1280 and were comparable to the conventional open tubular columns. Figure 3c shows a typical temperature programmed separation of seven compounds.

The short 1.5 m long GC columns made rapid analysis possible with adequate retention and relatively high resolution (1.7–1.8). A shorter column is known to provide higher sample concentra-

Table 1. Chromatographic Data of the CNT-Coated GC Column (1.5 m long) with Select Compounds, Where *k'* is the Capacity Factor and *N* is the Number of Theoretical Plates

	boiling point (°C)	<i>k'</i> (CNT-coating)	<i>N</i>
methanol	64.7	1.02	1820
hexane	69	0.82	1710
ethanol	78	2.05	1920
carbon tetrachloride	76.76	1.21	1620
benzene	80	1.59	1724
acetonitrile	81.6	1.67	1780
propanol	97	3.62	1684
toluene	111	2.59	1450
1-butanol	117	5.21	1675
<i>m</i> -xylene	139	5.02	1684
phenol	182	5.97	1520
naphthalene	217.9	7.16	1350

tions at the detector and therefore enhanced sensitivity.^{39–41} The performance of the CNT column was compared to a commercial DB-624 (0.53 mm i.d., J&W Scientific) column of similar length. Elution orders of the compounds in both columns were identical (Figure 4). Figure 4 shows that under the same conditions only three peaks were observed in the DB-624 column, where methanol and ethanol could not be resolved. However, these compounds were well resolved in the CNT-coated column. The resolution of the first two peaks on the DB-624 column was 1.0, while that on the CNT column was 1.7 (baseline resolution). The elution of all the compounds from the CNT column was completed within 2.3 min, and the corresponding time on the DB-624 column was

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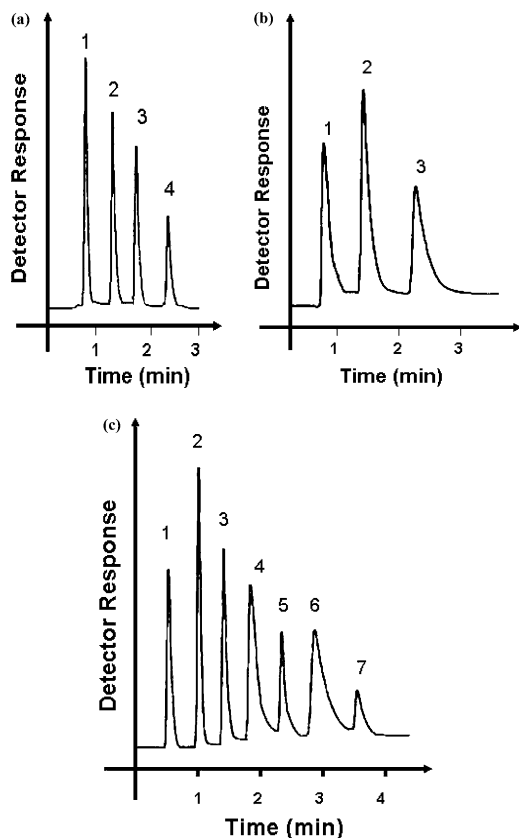


Figure 3. Chromatographic separations using the CNT-coating column: (a) separation of hexane (1), carbon tetrachloride (2), acetonitrile (3), and ethylbenzene. The temperature program was as follows: 50 °C for 0.5 min, ramp at 20 °C min⁻¹ to 100 °C at a carrier gas flow rate of 2.5 mL min⁻¹, and injection volume was 5 μ L. (b) Separations of benzene (1), toluene (2), and *m*-xylene. The temperature program was as follows: 100 °C for 1 min, ramp at 10 °C min⁻¹ to 160 °C at a carrier gas flow rate of 3.0 mL min⁻¹, and injection volume was 5 μ L. (c) Separations of methanol (1), ethanol (2), carbon tetrachloride (3), acetonitrile (4), *m*-xylene (5), phenol (6), and naphthalene. Temperature program was as follows: 50 °C for 1.0 min, ramp at 20 °C min⁻¹ to 100 °C and held 1 min, then ramp at 35 °C min⁻¹ to 210 °C at a carrier gas flow rate of 3.0 mL min⁻¹, and injection volume was 5 μ L.

1.2 min. Therefore, the CNT column had significantly higher capacity than the DB-624 column.

The van't Hoff plot of $\log k'$ as a function of $1/T$ for ethanol and benzene is shown in Figure 5. The linear plot (with correlation coefficients of 0.99) suggests that the separation followed classical chromatographic behavior.⁴² Similar behavior has been reported before with other nanoscale stationary phases like gold nanoparticles^{43,44} and CNT phases prepared in our laboratory.^{21,22,30} Since there was no noticeable change in slope, it is assumed that there was no phase transition.⁴⁵ Figure 6 shows the Van Deemter plot for the column with benzene at 110 °C. The minimum height equivalent theoretical plate (HETP) was 0.087 cm, and the optimum flow rate of the carrier gas was 3.0 mL min⁻¹, which is

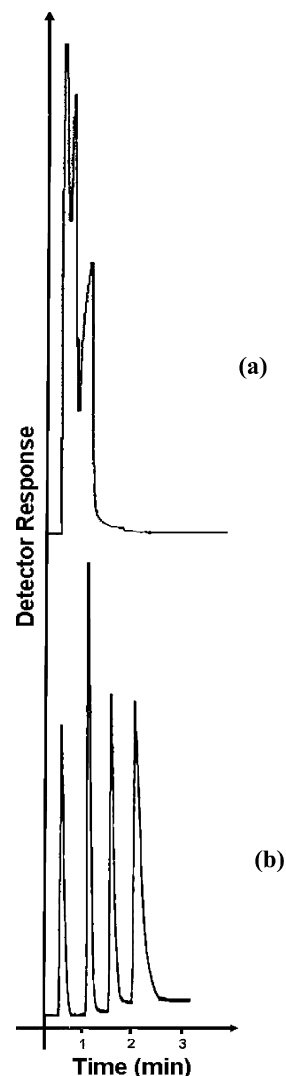


Figure 4. Chromatograms of methanol, ethanol, propanol, and 1-butanol: (a) 1 m DB-624 column, (b) CNT-coated column under similar conditions. Temperature program was as follows: 50 °C for 1.0 min, ramp at 20 °C min⁻¹ to 100 °C and held 1 min at a carrier gas flow rate of 3.0 mL min⁻¹, and injection volume was 5 μ L. Split injection (20:1, 210 °C), Detector, FID, 250 °C.

typical for columns of such internal diameter. The minimum HETP less than or equal to 1 cm is indicative of a high-performance open tubular GC system.^{46,47}

The reproducibility and stability of the CNT coating was also evaluated. Table 2 presents the run-to-run ($n = 5$) and day-to-day ($n = 10$) RSD values obtained for the retention times and peak width at half height. The RSD of 1–2% in retention time was at par with commercially available columns^{48–50} and is a testimony of uniform CNT deposition along the column. These values are also in good agreement with our previously reported CNT-based

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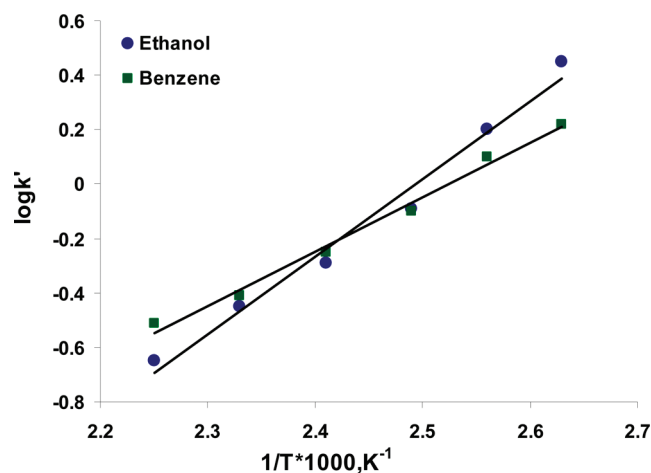


Figure 5. Van't Hoff plot of variation in capacity factor (k') with temperature (T) for ethanol and benzene.

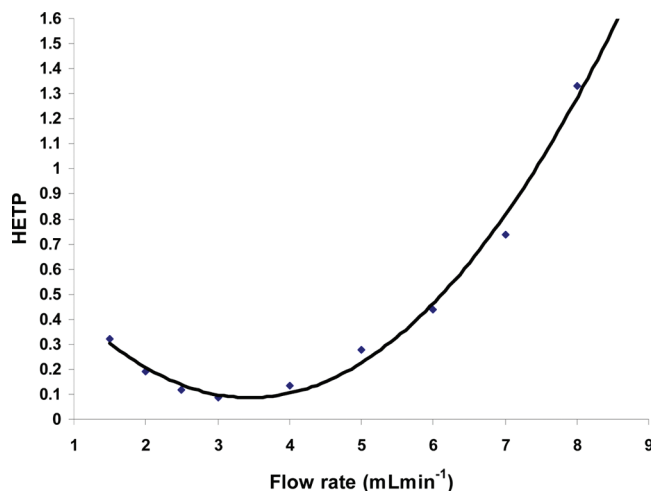


Figure 6. Van Deemter plot for benzene (H_{min} : 0.087 cm at 3.0 mL min⁻¹).

stationary phases²² synthesized via ethylene CVD. Three CNT-coated columns were prepared under identical conditions, and the capacity factors were obtained for selected solutes (Table 3). The low RSD values bear evidence to the fact that with ethanol as a carbon source for CVD of CNT, deposition was a reliable and reproducible technique.

Table 2. Run-to-Run and Day-to-Day Reproducibility for CNT Coating As the Stationary Phase

compound	RSD (%)			
	run-to-run (<i>n</i> = 5)		day-to-day (<i>n</i> = 10)	
	retention time (<i>t_R</i>)/min	peak width at half height (<i>w_h</i>)/s	retention time (<i>t_R</i>)/min	peak width at half height (<i>w_h</i>)/s
ethanol	1.21	1.53	1.56	2.03
carbon tetrachloride	1.54	1.31	2.01	2.31
benzene	1.21	1.98	2.31	2.16
acetonitrile	1.81	1.57	1.96	2.37
toluene	1.36	1.53	1.58	2.33

Table 3. Evaluation of Capacity Factors (k') for Column–Column Reproducibility

columns	capacity factor (<i>k'</i>)		
	ethanol	<i>m</i> -xylene	naphthalene
1	2.05	5.15	7.17
2	2.16	5.23	7.29
3	2.23	5.09	7.34
	% RSD 2.30	% RSD 1.09	% RSD 1.04

CONCLUSIONS

Ethanol CVD was an effective one-step process for the synthesis and self-assembled CNT stationary phases for open tubular GSC columns. The CNT distribution and morphology was quite different from those synthesized previously by ethylene CVD. The CNTs were not vertically aligned but lay flat out on the tube surface in random noodle-like configuration. The CNTs were highly pure with little amorphous or other carbonaceous impurities. The stationary phase demonstrated relatively high resolution for compounds with diverse polarity and volatility, where the number of plates per meter varied between 900 and 1280 per meter.

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