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PAPER

# Altering the polarity of self-assembled carbon nanotubes stationary phase *via* covalent functionalization

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We present for the first time that self assembled carbon nanotubes (CNTs) can be functionalized to alter their polarity and chromatographic behavior. The nanotube phase was synthesized *via* ethanol chemical vapor deposition (CVD) and functionalized by acid oxidation. Compared to an equivalent CNT column, the functionalized nanotubes (f-CNTs) showed strong retention and enhanced separation for polar organics such as alcohols, where the capacity factor increased by more than 100%, and the number of plates per metre increased by as much as 60%. The f-CNTs phase showed classical chromatographic behavior and good reproducibility. This is an important first step toward the development of diverse functionalized CNT columns.

## 1. Introduction

Carbon nanotubes (CNTs) have some extraordinary sorption properties which make them excellent sorbents for a variety of analytical applications.<sup>1–3</sup> Studies have shown that CNTs are highly effective gas and aqueous phase sorbents and can trap a wide range of molecules from H<sub>2</sub>, and methane to large semi-volatiles.<sup>4–8</sup> Therefore, they demonstrate tremendous versatility as far as analytical sorbents are concerned. Several reviews have been published on their applications in solid-phase extraction (SPE), solid-phase microextraction (SPME),  $\mu$ -SPE and microconcentrators.<sup>9–12</sup>

CNTs have been used as chromatography stationary phases. Their high capacity,  $\pi$ - $\pi$  stacking interactions with aromatic and unsaturated compounds, combined with high thermal stability, make them attractive as gas solid chromatography (GSC) stationary phases.<sup>13–20</sup> The superior sorption properties of CNTs have also been utilized in liquid chromatography and capillary electrophoresis to provide better resolution and enhanced signal-to-noise ratio.<sup>21–23</sup>

A major advantage of CNTs when applied to chromatographic separation is that they can be self-assembled on the walls of a tube *via* chemical vapor deposition leading to the formation of an open tubular column, which is associated with larger number of plates per metre.<sup>16,17,20,24</sup> Both single and multi-walled carbon nanotubes have been self-assembled on the tube surface and different precursors have been used providing different advantages.<sup>16,17</sup> While CNT stationary phases have shown excellent performance, they are non polar in nature and it

is anticipated that the alternation of their polarity would greatly enhance their performance.

Functionalization of CNTs has been effectively used to alter dispersibility in different solvents, their compatibility with other materials, such as polymers, and even for developing substrates for cell growth.<sup>25–29</sup> Functionalization of CNTs also offers the unique opportunity of tailor making sorbent properties and has been used in air sampling<sup>30</sup> and in packed GC columns.<sup>31</sup> The objective of this paper is to study the enhancement of polar compound retention *via* appropriate covalent functionalization of multi-walled carbon nanotubes (MWNTs) in a GC column fabricated *via* chemical vapor deposition self-assembly of CNTs.

## 2. Experimental

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, USA). Silico Steel 304 (Alltech, Deerfield, IL) metal capillary tubings (Restek, Bellefonte, PA, USA) were used for the self-assembly of CNTs.

The CVD system was used for the fabrication of GC columns and has been described before<sup>24</sup> and is shown in Fig. 1. Ethanol was used as the carbon source. The GC columns were fabricated on 1–2 m long, 0.53 mm i.d. 304 stainless steel tubing, which was coiled and placed inside the tube furnace. The tubes were washed with acetone to remove any particles/impurities, dried, and the steel surface was prepared at 550 °C with air flow of 10 mL min<sup>−1</sup> for 30 min. Typical CVD time was between 15–60 min at 700 °C under the argon flow rate of 10 mL min<sup>−1</sup>. Check valves (R. S. Crum & Co., Mountainside, NJ, USA) were placed on both lines to restrict backflow. Experiments were carried out in a fume hood and necessary safety precautions were taken as ethanol was used at high temperature. After the CNT deposition, the columns were heated at 200 °C in air for 1 h

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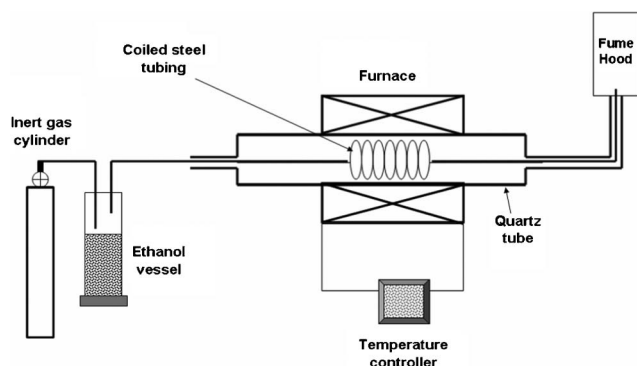


Fig. 1 Schematic diagram of CVD system.

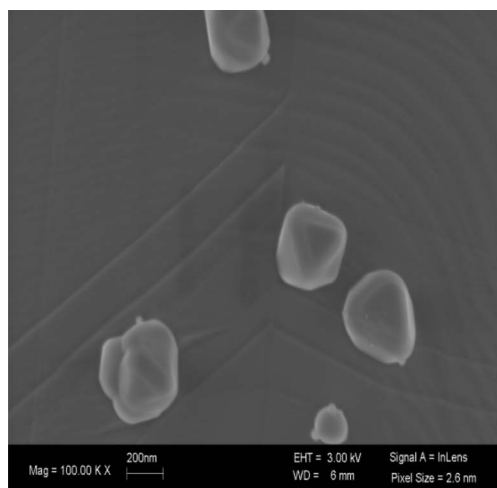
to oxidize amorphous carbon and other impurities generated during the process. Later, the column was heated in argon at 425 °C for 1 h to anneal and remove any low-boiling impurities.

## 2.1. Functionalization of the self-assembled CNT-stationary phase

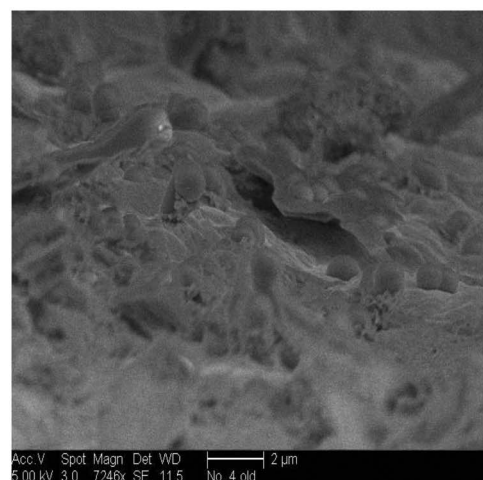
After oxidative purification of the CNT-column, functionalization of the CNT-stationary phase was carried out as follows. The CNT-column was filled with a 50 : 50 mixture of relatively dilute  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and the column was placed in beaker containing same acids, so that it was totally submerged in the acids. This beaker was heated for 10–15 min to 150 °C. The column was removed, washed with water and placed in a flow of Ar and annealed at 250 °C for 30 min. In order to ensure that the CNT coating was uniform, 1 cm-long segments were cut at different equidistant locations and analyzed using a Leo 1530 VP (Carl Zeiss SMT AG Company, Oberkochen, Germany) field emission scanning electron microscope.

## 2.2. Gas chromatography

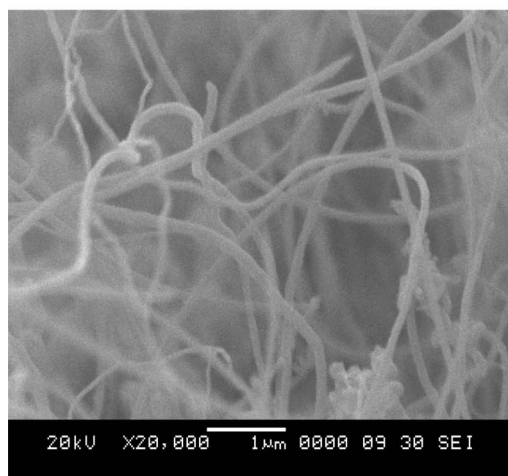
A gas chromatograph (model Varian 3400, Varian Inc. Palo Alto, CA, USA) equipped with a conventional flame ionization



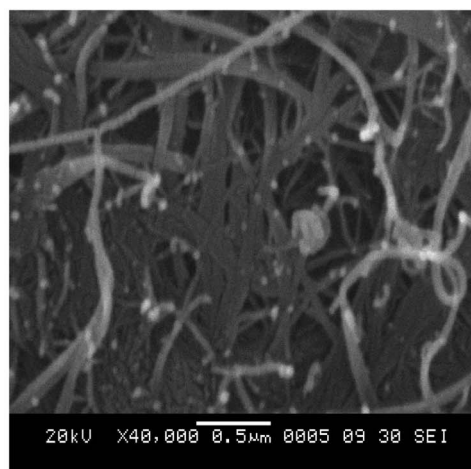
(a)



(b)



(c)



(d)

Fig. 2 SEM images (a) original steel tubing surface, (b) surface after air oxidation at 550 °C, (c) CNT-coating after ethanol CVD, (d) CNT-coating after functionalization

**Table 1** Comparison of chromatographic data on CNT and f-CNT column, where,  $k$  is the capacity factor and  $N$  is the number of theoretical plates per metre

Compounds		Boiling point (°C)	$k$		$N$	
			CNT-Column	f-CNT-Column	CNT-Column	f-CNT-Column
Polar	Methanol	64.7	1.02	1.98	1213	1820
	Ethanol	78	2.05	3.76	1280	1920
	Propanol	97	2.62	5.89	1122	1684
	1-Butanol	117	3.21	7.12	1116	1674
Non-polar	Benzene	80	1.59	—	1133	—
	Toluene	111	2.59	—	966	—
	Xylene	139	5.02	—	1125	—

(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  $\mu$ L Hamilton model 701 microlitre syringe (Hamilton Co., Reno, NV, USA) through a split-splitless injection port. Injector and detector temperatures were set at 250 °C, and a typical injection volume was 1.0  $\mu$ L unless otherwise specified. All injections were performed in the split mode with the split ratios varying between 1 to 20.  $N_2$  was used as a carrier gas with a flow rate of 3 mL min<sup>-1</sup>. The FID gases comprised of air flow at 300 mL min<sup>-1</sup> and hydrogen at 30 mL min<sup>-1</sup>. All GC measurements were repeated at least three times.

### 3. Results and discussion

Mechanism of CNT growth *via* ethanol CVD has been described before and is not discussed here for brevity.<sup>24</sup> The steel tubing was made catalytically active by air oxidation. SEM images of steel tubing surface before and after air oxidation are shown in Fig. 2 (a, b) respectively. Similarly, SEM images of CNTs after ethanol CVD and functionalization carbon nanotubes (f-CNT) are shown in Fig. 2 (c, d) respectively. Multiple GC columns were made and analyzed to check the reproducibility of the process.

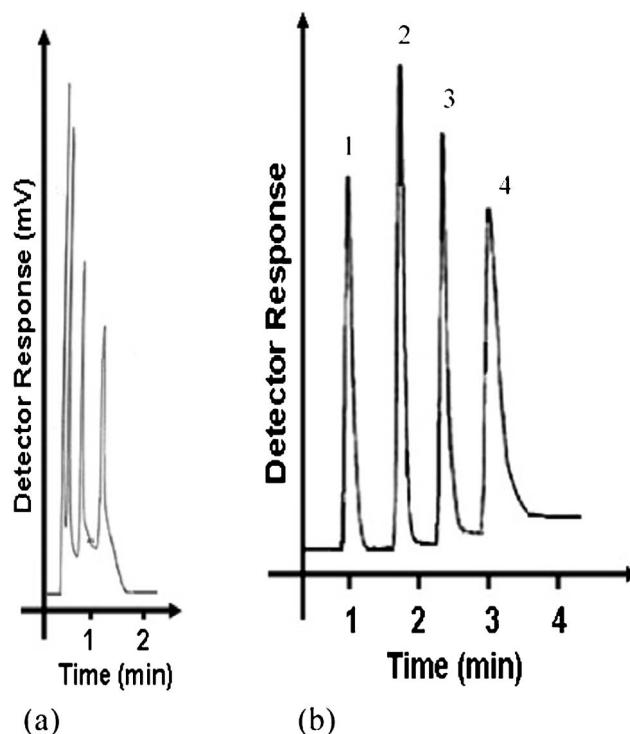
To incorporate functional groups into the CNT stationary phase uniformly in the capillary column, it was necessary to evenly introduce of acidic solution to CNTs. Several acid oxidative methods have been developed to functionalize the CNTs to generate carboxylic groups on the surface; these include sonication and microwave treatment.<sup>32–38</sup> However, functionalization of self-assembled CNTs on a steel surface is complicated by the fact that the metal leaches out of the steel tubing. SEM images of f-CNT-coatings in Fig. 2 d reveal that indeed some of the components were leached from the metal and some discrete nano scale particles are deposited on the CNTs' surface. However, the CNT is not completely coated and the surface is available for sorption of analytes. Other images at different spots along the column are not presented here for brevity, but they showed similar morphology.

#### 3.1. Chromatography on f-CNT

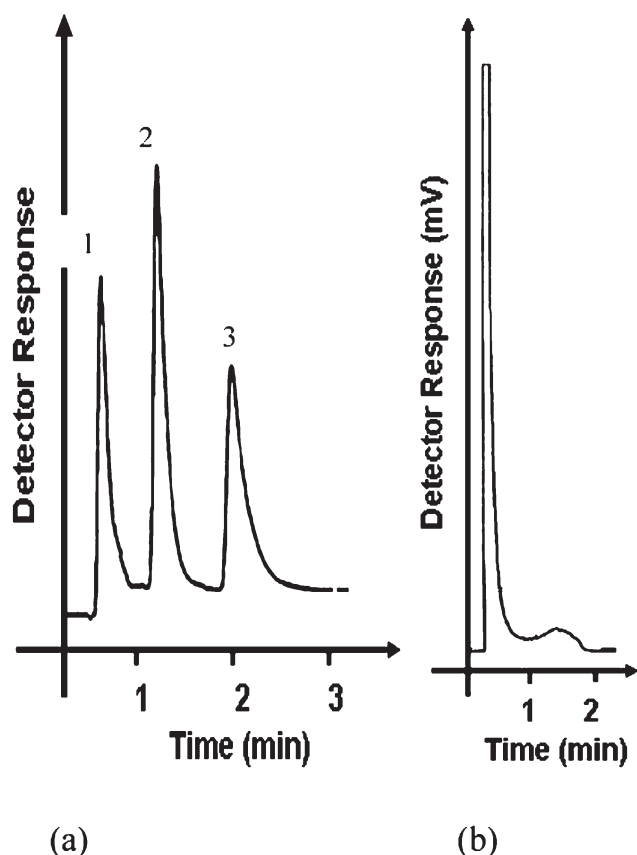
The influence of functionalization on the separation efficiency of the f-CNT column was evaluated with selected polar (alcohol) and non polar (aromatic) organic compounds, whose boiling points ranged from 64.7 to 117 °C (Table 1). Chromatograms on as prepared and functionalized columns are presented in

Fig. 3 (a, b). Although both columns were able to separate polar analytes, under the same chromatographic conditions, the retention time on the f-CNT column was significantly higher (nearly twice), therefore it was clear that these analytes were more strongly retained. On the other hand, when the nonpolar compounds namely benzene, toluene and xylene were injected into both columns, the separation was excellent on the CNT column (Fig. 4a) and in line with previous reports,<sup>16,24</sup> but the f-CNT column showed no separation (Fig. 4b). This implied that the CNT surface had a high density of carboxylic groups, and the polarity was quite high.

Comparison between chromatographic parameters of the pristine and carboxylated CNT for selected compounds are as listed in Table 1. These were obtained under isothermal conditions and at an optimum flow rate of 3 mL min<sup>-1</sup>. The number of theoretical plates ( $N$ ) per metre for the polar compounds



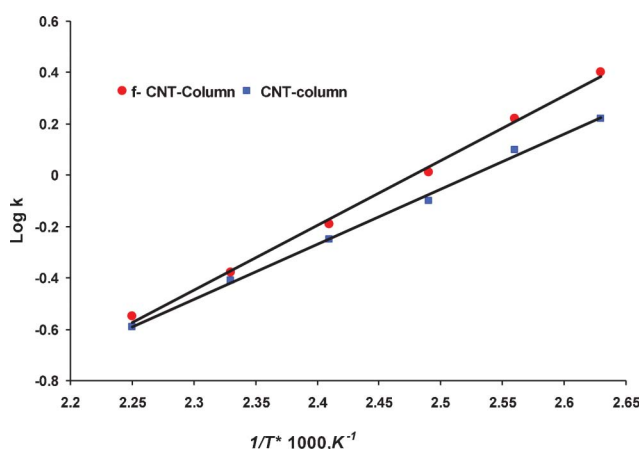
**Fig. 3** Chromatographic separations of methanol, (1), ethanol, (2), propanol, (3) and 1-butanol (4). Temperature program was as follows, 50 °C for 0.5 min, ramp at 20 °C min<sup>-1</sup> to 100 °C at a carrier gas flow rate of 2.5 mL min<sup>-1</sup> and injection volume was 5  $\mu$ L. (a) CNT-coating column (b) f-CNT-coating column.



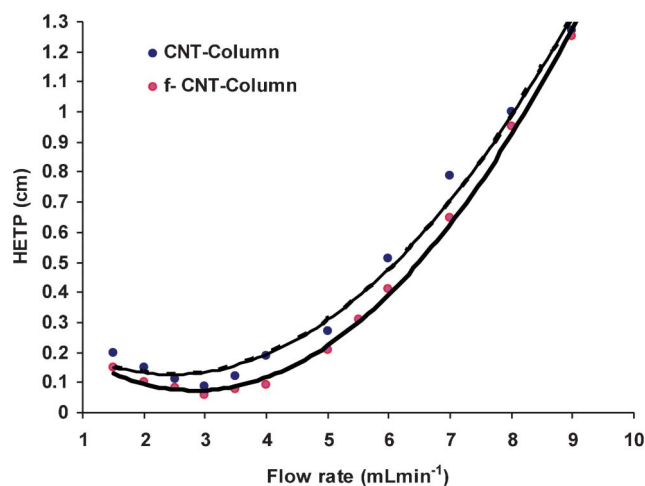
**Fig. 4** (a) Chromatogram of benzene (1), toluene (2), and m-xylene (3) on: (a) CNT column, (b) chromatogram on f-CNT-column. The temperature program was as follows, 100 °C for 1 min, ramp at 10 °C min<sup>-1</sup> to 160 °C at a carrier gas flow rate of 3.0 mL min<sup>-1</sup> and injection volume was 5 µL.

varied between 1117 to 1280 on CNT column, whereas the range on f-CNT was between 1675 to 1920. This was the equivalent of 50% increase in the number of plates per metre, and this was attributed to strong interactions of polar analytes with the functionalized surface.

The Van't Hoff plots of log *k* as a function of 1/*T* for ethanol on both columns are shown in Fig. 5. The linear plot (with



**Fig. 5** Van't Hoff plot of variation in capacity factor with temperature for ethanol on (a) CNT and (b) f-CNT column.



**Fig. 6** Van Deemter plot for propanol; CNT-column (Hmin: 0.089 cm) and f-CNT-column (Hmin: 0.059 cm).

correlation coefficients of 0.99) on both columns suggests that the separation followed classical chromatographic behavior and well in accordance of previous report.<sup>24</sup> Fig. 6 shows the Van Deemter plot for the column with ethanol. The minimum height equivalent theoretical plate (HETP) was 0.089 cm for CNT and 0.059 cm for f-CNT column. The reduction of 0.03 cm represents an significant enhancement.

The reproducibility and stability of the f-CNT-column was also calculated. 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 in retention time was less than 1% for polar analytes on the f-CNTs column, which indicated that the stationary phase was quite stable. Three CNT columns were functionalized under the same conditions, and the capacity factors were obtained for selected polar analytes. The low RSD values (0.94–1.04) show that with acidic functionalization process was a consistent and reproducible.

#### 4. Conclusions

In summary, it was possible to functionalize self-assembled CNTs by conventional acid treatment. The functionalization altered separation behavior of the CNTs phase quite dramatically. The increase in capacity factor and plates per metre was quite significant for the polar compounds studied here. The oxidized phase showed excellent structural and functional integrity, number of plates per metre were as high as 1920 and

**Table 2** Reproducibility on f-CNT-coating

Compound	RSD (%)			
	Run-to-run ( <i>n</i> = 5)		Day-to-day ( <i>n</i> = 10)	
	Retention time ( <i>t</i> <sub>R</sub> ) min	Peak width at half height ( <i>w</i> <sub>0.5</sub> ) sec	Retention time ( <i>t</i> <sub>R</sub> ) min	Peak width at half height ( <i>w</i> <sub>0.5</sub> ) sec
Methanol	0.77	1.53	0.66	2.03
Ethanol	0.54	1.31	0.61	2.31
Propanol	0.81	1.98	0.87	2.16
1-Butanol	0.94	1.57	0.96	2.37



RSDs were less than 1. The functionalized phase was relatively ineffective for nonpolar compounds. The advantage of this approach is that self-assembled CNTs can be altered to change selectivity for different classes of analytes.

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