Nanotube GC Sensor

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On-Chip Micro Gas Chromatograph Enabled by a Noncovalently Functionalized Single-Walled Carbon Nanotube Sensor Array**

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Single-walled carbon nanotubes (SWNTs) are quasi-1D electronic materials consisting only of surface atoms whose electrical properties can be directly modulated by molecular adsorption.[1] This environmental sensitivity has been utilized to engineer sensor arrays with electrical responses to parts-per-billion (ppb) doses of organic vapors.[2–6] Polymers,[2,7–9] metal nanoparticles,[10,11] and DNA[12] have been reported as functional materials for enhancing the selectivity of such systems. A central problem with the majority of these sensor arrays, including a recent SWNT chemi-capacitor arrangement,[4] is that molecular adsorption is irreversible upon exposure to a wide range of analytes. To be clear, we define reversible adsorption not as the ability to be externally or manually regenerated, but rather the spontaneous desorption of analyte when the chemical potential gradient has been removed. By this criterion, strong electron donors or acceptors appear to adsorb onto bare single-nanotube or network devices irreversibly at room temperature for the vast majority of systems examined in the literature.[2–5,8,9,11,13–15] In later publications, some of these same systems demonstrate reversible sensor responses from the same analytes,[12,16–18] thus underscoring a poor understanding of what determines molecular reversibility. No examination of the disparity has been reported to date.

Previously, we demonstrated that irreversible electrical responses upon $SOCl_2$ exposure (a model electron acceptor) were indeed attributed to irreversible analyte adsorption.[13] We have recently elucidated design rules and have identified noncovalent chemistries that transition this irreversible binding into reversible responses that appear tunable.[19] Herein, we show that the ability to engineer molecular reversibility of adsorption enables the development of new types of nanoelectronic devices for analyte detection using microelectromechanical system (MEMS)-based micro gas chromatography (μGC). The specific combination of the SWNT sensor and μGC column is not possible with previously described systems, many of which show an irreversible response. We demonstrate the unprecedented reversible detection of as few as 10^9 molecules of dimethyl methylphosphonate (DMMP), a nerve agent simulant, at the end of a μGC column.

An interdigitated electrode design was chosen to maximize the nanotube surface area for analyte adsorption, as predicted from our model.[13,20] A SWNT network was formed across the electrodes through ac dielectrophoresis (Figure 1a). Polypyrrole (PPy), an amine of $pK_b \approx 5.4$,[21] was selected as a functionalization material for DMMP binding.[22] A slight decrease in conductance (G) was observed upon

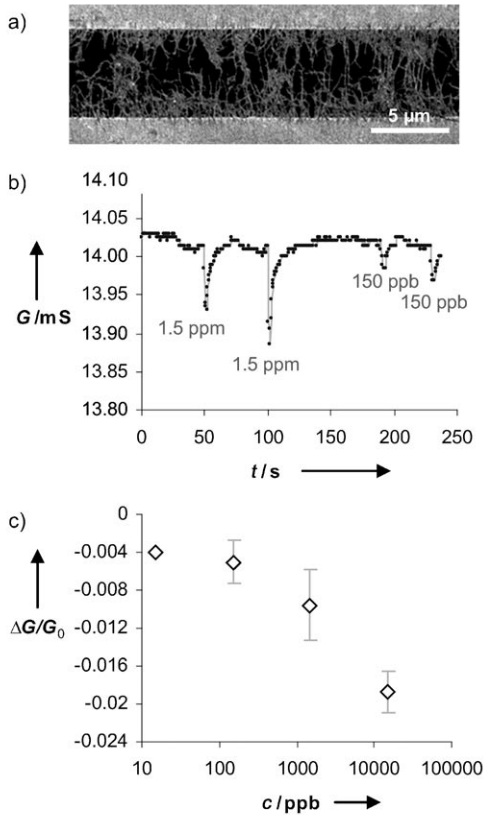

Figure 1. SWNT sensor fabrication and testing. a) Scanning electron microscopy (SEM) image of a dielectrophoretically deposited SWNT network. b) Reversible conductance response from a PPy-functionalized SWNT sensor upon exposure to 1-mL DMMP pulses. c) DMMP response curve.

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functionalization. The sensor response in an open-air environment was tested first. Control experiments with only PPy on the electrode gap showed no response to DMMP. Figure 1 b shows a typical change in sensor conductance upon exposure to 1-mL pulses of DMMP vapor. The responses fall within the ppb range and are completely reversible, with full width at half maximum (FWHM) of only about 4 s. The decrease in conductance is attributed to electron-donating DMMP molecules adsorbed on p-type semiconducting SWNTs.[5] A response curve for 1-mL analyte pulses is generated from four sensors (Figure 1 c). The response from unfunctionalized sensors is reversible, but the sensitivity is enhanced by three orders of magnitude after PPy functionalization with the reversibility retained.

Using our model,[20] we were able to extract kinetic and thermodynamic parameters, such as the adsorption rate constant (k), desorption rate constant (k_{-1}), equilibrium constant ($K = k/k_{-1}$), and therefore the Gibbs free energy of adsorption (ΔG_{ad}). The desorption part of the sensor signal ($S = \Delta G/G_0$, where G_0 is the initial conductance) is first fitted to Equation (1) to obtain $k_{-1} = 0.525\ \mathrm{s}^{-1}$. S_0 represents the signal when the analyte is removed. The maximum signal ($S_{max} \approx -0.176$) upon saturation is estimated by exposing the sensor to a high concentration of DMMP vapor. Fitting the adsorption part to Equation (2), at an analyte concentration C_a, gives $k = 3.66 \times 10^{-5}\ \mathrm{ppb}^{-1}\,\mathrm{s}^{-1}$ and $K = 6.98 \times 10^{-5}\ \mathrm{ppb}^{-1}$. $\Delta G_{ad} = -0.286$ eV is then extracted from Equation (3), where R and T denote the gas constant and temperature, respectively. ΔG_{ad} determines how favorable the adsorption is at equilibrium.

$$S(t) = S_0 \exp[-k_{-1}t] \tag{1}$$

$$S(t) = S_{max} \frac{C_aK}{1+C_aK}\left(1-\exp\left[-\frac{1+C_aK}{K}kt\right]\right) \tag{2}$$

$$\Delta G_{ad} = -RT \ln K \tag{3}$$

A parameter directly related to the DMMP desorption rate, and therefore the sensor reversibility, is k_{-1}. The value of $0.525\ \mathrm{s}^{-1}$, improved by three orders of magnitude compared to $k_{-1} = 3.67 \times 10^{-4}\ \mathrm{s}^{-1}$ from a previously reported partially irreversible system,[5,20] quantifies the comparatively rapid signal recovery from the sensor.

Tuning the array to exact a rapid, reversible response with high sensitivity enables new applications for real-time, dynamic detection by these systems. As mentioned previously, one example is a reversible SWNT array coupled to the outlet of a μGC column. Chromatographic separation and detection remains the analytical standard for the detection of diverse classes of organic molecules. Testing cross-sensitivity is therefore unnecessary with this design. Our approach eliminates the need to engineer selective binding sites for small-molecule analytes for SWNTs, a difficult problem only solved in specialized cases for H_2, H_2S, and CH_4 by using metal nanoparticles[10,11] and for CO_2 using a starch/polyethyleneimine mixture.[7] Target specificity is achieved through a μGC column in which the analytes are screened by their retention time. Another advantage of such a microfluidic arrangement lies in the exceedingly small footprint ($800 \times 800\ \mu m^2$) for molecular discrimination by column chromatography and detection with a rapidly transducing electronic array. We demonstrate that the SWNT network, when chemically treated as described above, has a response that is rapid and sensitive enough to reversibly detect DMMP in real time from the end of a μGC column.

Figure 2 a outlines the fabrication and assembly of the μGC column. An SEM image of the column cross section is shown in Figure 2 b. The μGC column is connected to the injection port of a conventional benchtop gas chromatograph to ensure precision in measurement of the detection limit (Figure 2 c). The outlet is then carefully aligned above a PPy-treated SWNT sensor (Figure 2 d). With H_2 carrier gas flowing at 40 psi, a DMMP headspace (2 μL) was manually injected (< 0.3 s) at a 7:1 split and the conductance was monitored. The injector and column temperature were 250 and 30 °C, respectively.

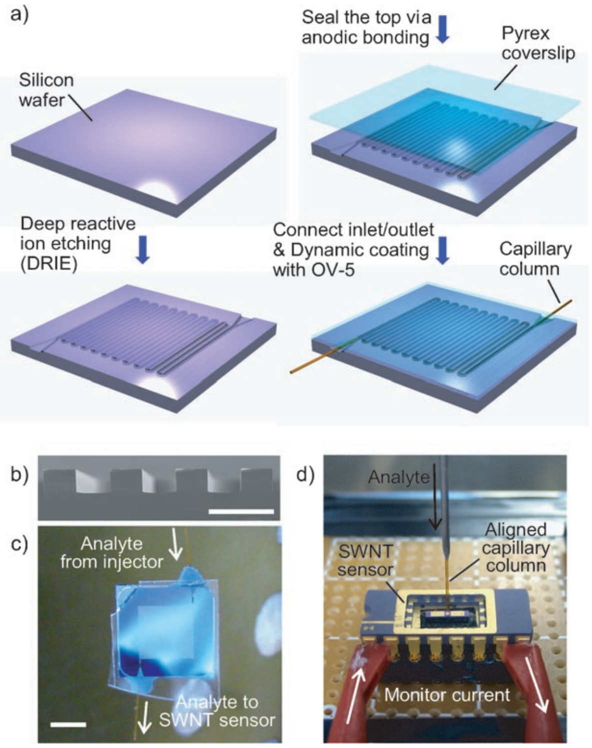

Figure 2. a) Fabrication of a μGC column. OV-5 = 5% diphenyl/95% dimethylpolysiloxane. b) SEM image of a μGC column with a $100 \times 100\ \mu m^2$ channel cross section (scale bar = 200 μm). c) A μGC column connected to the injection port. The injected analyte molecules flow through the μGC column and to the SWNT sensor (scale bar = 5 mm). d) A SWNT sensor at the end of a μGC column. Analyte flows through an aligned capillary column to the SWNT sensor.

The sensor response (Figure 3 a) is negative and reversible with FWHM ≈ 26 s. The 150-ppb pulse corresponds to approximately 10^9 DMMP molecules, a number that was confirmed by the downstream flame ionization detector (FID). The ability of our experimental approach and detection limits to be independently verified by GC-FID is unique,

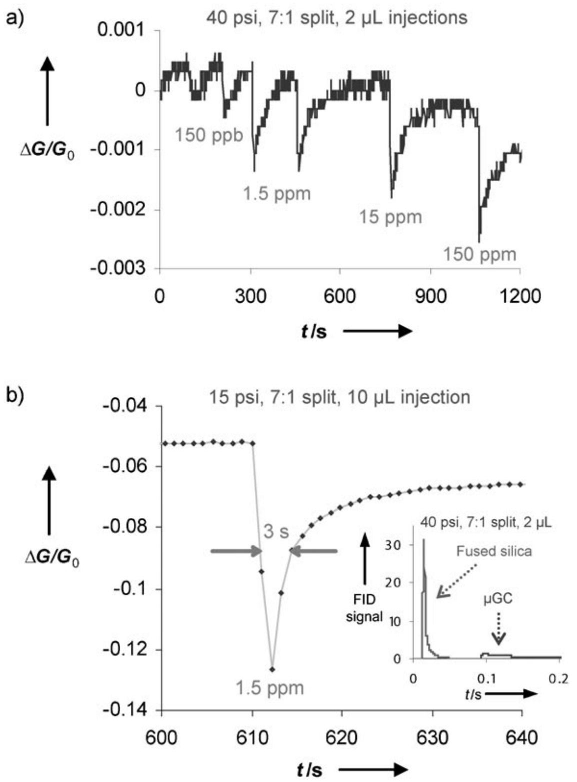

Figure 3. Integration of a reversible SWNT sensor with a µGC column. a) DMMP pulses through the µGC column detected by a PPy-functionalized sensor. A 150-ppb pulse corresponds to 10^9 DMMP molecules. b) Response of a PPy-functionalized sensor to a DMMP pulse through a conventional fused-silica column. The peak is much sharper (FWHM ≈ 3 s) than that from the µGC column (FWHM ≈ 26 s). This is because of peak broadening in the µGC column, as confirmed by the FID signal (inset).

and provides a high level of confidence in the reported absolute and relative detection limits. We note that the direct electrical transduction of 10^9 molecules in this manner has not been demonstrated before with any analytical platform.

Figure 3 b shows a response of the SWNT array to 10 µL of 1.5 ppm DMMP at a 7:1 split at 15 psi using a 3-m-long commercial fused-silica column. The FWHM is as short as 3 s. The extracted $k_{-1} = 0.325\ \mathrm{s}^{-1}$ is larger by an order of magnitude than $3.25 \times 10^{-2}\ \mathrm{s}^{-1}$ from the µGC column response. This result suggests that the broad peaks in Figure 3 a arise from peak broadening in the µGC column, which is attributed to the imperfections in microfabrication, microfluidic connections to and from the microchannel chip, and column wall surface activity. This suggestion is confirmed by a much broader FID signal from a µGC column than from a conventional fused-silica column (40 psi, 7:1 split, 2 µL injection; Figure 3 b, inset). A slight baseline drift is caused by analyte adsorption on strong binding sites, such as interstitial channels and grooves.[19]

In summary, we have utilized PPy functionalization on a dielectrophoretically formed SWNT network for the detection of DMMP, a nerve agent simulant. Our sensor is highly sensitive and completely reversible (self-regenerating) at the ppb level, which differentiates this system from existing irreversible examples in the literature. We show, for the first time, that such reversible sensors can be part of an integrated, microfluidic, and portable detector system. We have reversibly detected a pulse as small as 10^9 DMMP molecules at the end of a µGC column. Future work will examine the dynamic peak resolution of gas mixtures with this platform.

Experimental Section

An individual suspension of HiPco[23] SWNTs (Rice University, Run 107.1; HiPco = high-pressure CO conversion) in an aqueous solution of sodium dodecyl sulfate (1 wt.%) was deposited onto 5-µm-gap interdigitated gold electrodes by ac dielectrophoresis. PPy aqueous solution (5 wt.%, Aldrich) was then dropped onto the SWNT array and rinsed after 2 min. Changes in the sensor conductance upon exposure to DMMP vapor were monitored at 0.1 V (E5272A, Agilent) either in the open air without GC or in combination with GC (6890N, Agilent).

A µGC column was fabricated by the following steps. A 35-cm-long channel with $100 \times 100\ \mu\mathrm{m}^2$ cross sections was fabricated by deep reactive-ion etching (DRIE) of a silicon wafer. A pyrex coverslip was anodically bonded to seal the channel. A fused-silica column (internal diameter = 100 µm) was used to connect the µGC column from the injection port to the SWNT sensor. The column was then coated with about 100 nm OV-5 by dynamic coating (Figure 2 a).[24]

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