Chemically Functionalized Multi-Walled Carbon Nanotube Sensors for Ultra-Low-Power Alcohol Vapor Detection

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Abstract*—We have successfully chemically functionalized the multi-walled carbon nanotubes (MWCNTs) with COOH group by the method of oxidation and used AC electrophoresis to formed these bundles MWCNTs between Au electrodes on the Si substrate. We then demonstrated that these resistive elements are capable of detecting alcohol vapor using an ultra-low input power of only ~0.01µW. The sensors exhibit fast, repeatable, highly sensitive, and reversible response. Our results show that the resistances of the sensors vary linearly with alcohol vapor concentration from 5ppth to 100ppth (ppth = part per thousand). We can also easily reverse the initial resistance of the sensors by annealing them in real time at 100-250µA current within 1-6 minutes. We have experimental proof that the functionalized MWCNTs have a much higher sensitivity towards the alcohol vapor than the bare MWCNTs. Based on our experimental results, we prove that MWCNTs sensors, especially for those with proper functionalized groups, are sensitive to a wide range of alcohol vapor and potentially other volatile organic compounds, and are very attractive for commercialization due to their extreme low-power requirements for activation.

Keywords-low-power-sensing; CNT sensors; alcohol sensors; CNT functionalization; chemical sensors

I. INTRODUCTION

Micro sensors, based on physisorption or chemisorption, are playing an important role in chemical vapor detection for process control, home-land security, environmental monitoring and defense for their small size and accurate response [1-2]. These micro sensors are generally made of metal oxide and typically require high operating temperature for utmost performance, which is not very desirable for commercial products as this may cause high power consumption [3]. Over the last decade, carbon nanotubes (CNTs) have attracted substantial attention because of their unique structural, electronic, optical, thermal and mechanical properties [4]. These properties make them potential candidates for the building blocks of active nanostructure materials in nanoelectronics, field emission devices, and gas sensors [5-6]. Among these, gas sensing property of the CNTs at room temperature is very desirable for many kinds of applications [7]. It is due to the fact that they have nanosized morphology and high surface-to-volume ratio, which results in highly sensitive and rapid gas adsorption. Interaction with any gas molecules can change the electrical properties of CNTs. Also, they have fast response and good reversibility [8]. A research laboratory in USA [9] has demonstrated the chemical sensors based on individual single-walled carbon nanotubes (SWCNTs). Upon exposure to gaseous molecules such as NO_2 or NH_3, the electrical resistance of a semiconducting SWCNT is found to significantly increase or decrease. Also, M. Penza and co-workers from Italy [10] have fabricated and characterized surface acoustic waves (SAWs) sensors coated by either SWCNTs or MWCNTs for chemical detection of volatile organic compounds (VOCs).

Ethanol vapor has always been one of the most extensively studied gases for the gas sensors. It is because of the demand of small practical devices to detect alcohol on the human breath so that we can avoid intoxicated driving or to identify leaks in industrial distribution lines. SWCNTs in field-effect transistor (FET) geometry have been fabricated and its response towards the alcoholic vapor has shown to be significant by a research group in USA [11]. Another research team in Japan has demonstrated the feasibility of using Novolac resin to fabricate plastic optical fibre sensors to detect the alcohol vapor [12]. In this paper, we will present the possibility of using chemically functionalized MWCNTs (f-CNTs) as the sensing elements for the detection of alcohol vapor with ultra-low power consumption and high reproducibility. First, we will describe how we fabricate the f-CNTs and the sensors. Then we will show the I-V characteristics of the sensors and the experimental setup. Finally, the correlation between the sensors' resistance variation to alcohol vapor concentration and the sensitivity analysis for the sensors will be illustrated.

II. SENSOR FABRICATION

A. Fabrication of sensing element: f-CNTs

Commercially available MWCNTs (by chemical vapor deposition method, from Shenzhen Nanotech Port Co. Ltd, China) with length in 1-2µm and diameter in 10-20nm were employed in our experiment. The MWCNTs were purified by heating in a box furnace at 400°C for 2 hours at 1 atm. Then, purified MWCNTs were sonicated in 3:1 concentrated sulfuric acid and nitric acid for different time intervals. By this method, the MWCNTs can be oxidized and COOH groups will

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This project is supported by a grant from the Hong Kong Research Grants Council (CUHK4177/04E), a grant from the Shun Hing Institute of Advanced Engineering (BME 3/05) and RGC Direct Grant (CUHK 2060280).

be produced along the sidewall and the caps of the MWCNTs as shown in Fig. 1. We believe that the longer the time interval for the sonicating process, the larger the amount of COOH groups will be attached onto the MWCNTs. In this paper, the response of two types of f-CNTs, which are with sonicating time of 4 hours and 1 day respectively, are presented. After the sonicating process, the functionalized MWCNTs were collected by centrifuge and washed thoroughly with DI-water until the pH value was around 6~7. The resultant solid were then re-dispersed in propylene carbonate (PC) with density of 0.1 mg/ml for use. We think that with polar COOH groups attached onto the nanotube surface, the sensors will give stronger response towards the ethanol vapor as their absorption efficiency with these volatile organic molecules will be increased. It is due to the fact that these molecules can form dipole-dipole interaction (mainly hydrogen bonding) with the COOH groups connected on the MWCNTs.

B. Batch fabrication of the whole sensor

The Au microelectrodes were first fabricated on the Si-substrate by the lift-off process. The f-CNTs were then batch manipulated along the microelectrodes by AC electrophoresis with 16 peak-to-peak voltage and 1 MHz sine wave. The details of the fabrication process can be found in our previous paper [13]. The Si-substrate chip was then wire-bonded to a PCB board for later connection to the measuring unit. An airtight plastic cover was put on top of the sensor chip. Ten holes (diameter of 1.2mm) were drilled on the PCB board, which were around our sensor chip and under the plastic cover, for the outlet of the vapor.

III. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 2. The organic chemical we used for the alcohol solution was ethanol (from Merck Ltd., 99.9%). We prepared the alcohol solution by mixing different volume ratios of ethanol and DI-water (> 15megohm-cm). The sensors were tested with alcohol vapor concentration from 5ppth to 400ppth. The alcohol vapor was generated by directing a well-controlled flow of compressed air into the mixed solution. With the use of Keithley 2400 source meter, we studied the response of the sensors by a constant current configuration. All experiments were performed at room temperature of 23-25°C.

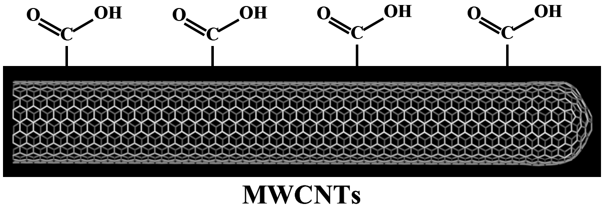

Figure 1. Multi-walled carbon nanotubes with COOH-group attached along the sidewall.

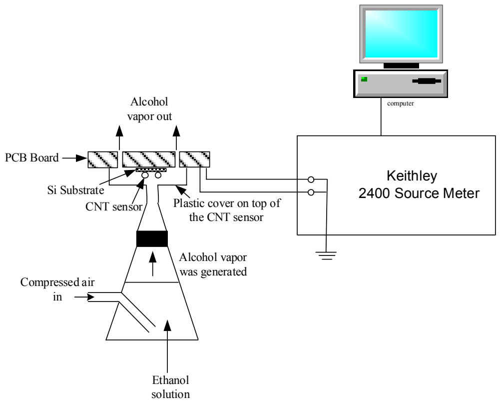

Figure 2. Schematic diagram showing the experimental setup for detecting alcohol vapor.

IV. CURRENT RESULTS

A. Electrical property of the f-CNTs sensors

Many research groups have investigated the electrical properties of individual CNTs in the last decades [14-15]. Many reports have illustrated their microwatt power characteristics. Although bundles of MWCNTs are complex networks of individual CNTs, they also show a similar behavior as stated in our previous paper [13]. But, from our experience, the performance of these bundles can have large variations and the MWCNTs we study now have chemically functionalized with COOH group. So, in this paper, we will first examine the I-V characteristics of two bundled f-CNTs sensors (4hr and 1day oxidized) using a constant current configuration. The results are shown in Fig. 3. The results are similar to other previous reports. Self-heating effect started at 100µA and 1V (35µA and 1.1V) for 4hr (1day) oxidized f-CNTs. It reveals that we can treat the bundled f-CNTs as a resistive element with ultra-low power requirement. In all experiment stated in the following, we activate the sensors at the linear region of 1µA with the power consumption of only ~0.006-0.04µW.

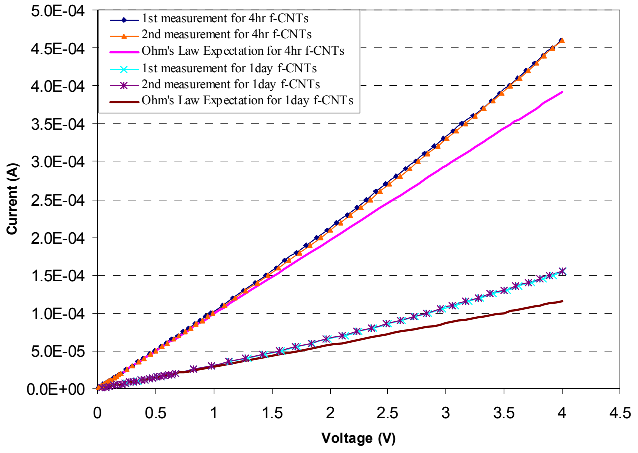

Figure 3. I-V characteristics of the f-CNTs bundles. Two repeated measurements were performed for each sensor to validate the repeatability. The straight line is the theoretical expectation using Ohm's law.

B. Typical Response of the sensors

Fig. 4 shows the observed response of the sensor at 25°C when an alcohol vapor of 100ppth was blown onto the sensor. The response of the sensor is very fast. As we can see in Fig. 4, a sharp response can be observed within 1s after we delivered alcohol vapor into the chamber. We filled the chamber with the alcohol vapor for 10s. We will relate the response of the sensors towards the ethanol vapor to the resistance change (ΔR).

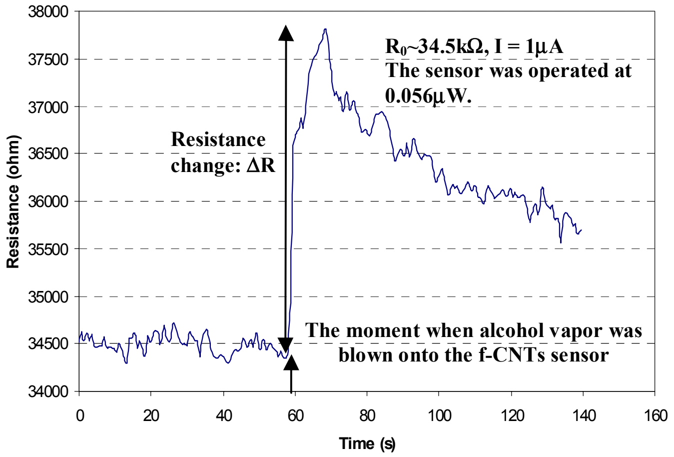

Figure 4. Observed resistance change of the 1day f-CNTs sensor with the introduction of 100ppth concentration of alcohol vapor.

C. Alcohol sensing ability of the sensors

Similar measurement like the one mentioned in Part B was carried out under the exposure of alcohol vapor from concentration of 5ppth to 100ppth. 2-3 cycles of data for two sensors (4hr f-CNT and 1day f-CNT) were done at each concentration as shown in Fig. 5. It shows that the sensors respond linearly with the alcohol vapor concentration with the resistance change. Both sensors have very good reproducibility for vapor of all concentration as most of the fluctuations are within 10% of the average values. In Fig. 6, the dependence of the sensitivity of the sensors on the concentration level of alcohol vapor was also shown and the sensitivity also increases linearly with the alcohol vapor concentration. We can clearly notice that the response of the 1day f-CNTs sensor is stronger than the 4hr f-CNTs. These results are reasonable as we expect that the longer the time interval for the oxidation process in acid, the larger the amount of COOH group will be attached to the MWCNTs, which results in more hydrogen bonding interaction and stronger response. We further compare these results with those using the bare MWCNTs. The response of the bare MWCNTs is much weaker than the f-CNTs and it confirms the COOH functional group is really more attractive towards the alcohol vapor. Although the f-CNTs sensors have stronger response with the alcohol vapor then the bare MWCNTs, they also have very good reversing ability as similar to the MWCNTs sensors [16]. We observed that they can also return back to their initial resistance after each experiment by annealing them at ~100 to 250μA for 1 to 6 mins.

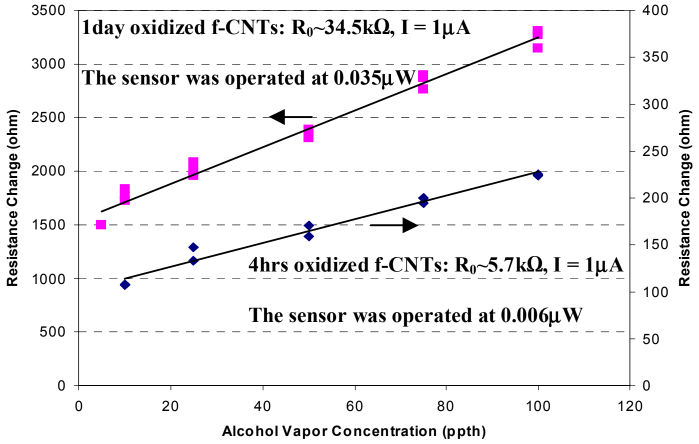

Figure 5. Response of the f-CNTs sensors to 10-s dose of alcohol vapor with concentration from 5-100ppth. Two to three cycles of measurements for each sensor were performed.

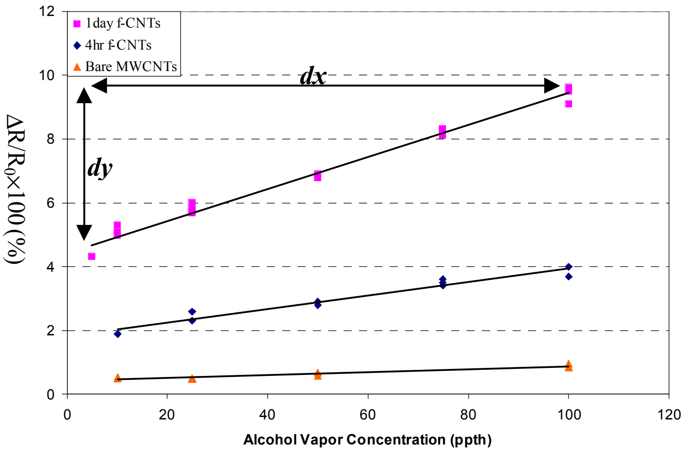

Figure 6. Measured relative percentage change of the resistance: $\Delta R/R_0 \times 100\%$, of 3 different sensors: bare MWCNTs, 4hr f-CNTs, and 1day f-CNTs. The results of the f-CNTs sensors are corresponding to the results in Fig. 5.

D. Sensitivity of the sensors

The sensitivity of alcohol sensors is defined as minimum input alcohol level that will create a detectable output change. It represents the minimum detectable alcohol level of the sensors, which is an important figure of merit of alcohol sensors. In this section, we will present the definition of sensitivity of the sensors, followed by the experiment of sensitivity analysis. At last, the result of sensitivity will be given. By definition, the sensitivity of sensors is given by:

$$sensitivity\,(\alpha) = \frac{system\ output\ noise\,(n_o)}{responsivity\ (\beta)} \qquad (1)$$

$$\text{responsivi ty}\,(\beta) = \frac{change\ in\ output\ \ (dy)}{change\ in\ input\ \ (dx)} \qquad (2)$$

As the absolute resistance of the alcohol sensors is not well controlled and changing form sensor to sensor, it will be more suitable to compare the responsivity (β) using the percentage change of sensors' resistance, hence, equation (2) can be rewritten as:

$$\text{responsivity}(\beta) = \frac{\text{percentage change of resistance}(dR/R_0)}{\text{Concentration change of alcohol}(dc)} \quad (3)$$

Using the experimental result of 1day f-CNTs in Fig. 6, we found that the responsivity of our sensor is about 0.037%/ppth. To find out the system output noise (n_o), we used the same experimental setup as before and measured the resistance of the sensor without applying the alcohol vapor. The sensor was kept under constant environment (25°C and 40% relative humidity). Theoretically, the resistance of the sensor should keep constant. However, in reality, the resistance of the sensor would have self-fluctuation due to noise. We took 1000 samples under this condition and computed the averaged output noise (n_o) using the following equation:

$$\text{averaged output noise in percentage}(n_o) = \left[\frac{\sum (R_o - R_i)^2}{1000}\right]^{\frac{1}{2}} / R \times 100\,\% \quad (4)$$

where R_o is the mean value of the sensor's resistance and R_i is the individual measurement. It was found out that the typical averaged output noise (n_o) of our sensor is 0.1-0.2%. Hence the sensitivity of our sensor in such measuring methodology is 2.37 - 4.74ppth. This means that the limit of detection for our 1day f-CNTs sensor is about 2.4 to 4.8 ppth.

It is possible that our measuring equipment and the environment may contribute to the system output noise. To investigate the noise contributed to the self-fluctuation of the sensor, we repeated the same experiment but replaced the f-CNTs sensor with a carbon film resistor with similar resistance. We have found out that the noise of this carbon film resistor is 0.01 – 0.02%, which is an order lower than the f-CNT noise. Hence, we can conclude that most of the noise in the f-CNTs sensor is inherent noise (noise that exists in the CNTs) rather than noise coming from measurement. Theoretically, resistors only have thermal noise. Thermal noise can be formulated by [17]:

$$\overline{v_n^{\,2}} = 4kTR\Delta f \quad (5)$$

where Δf is the measuring bandwidth, T is the temperature, and k is the Boltzmann constant. The measuring bandwidth is defined by equivalent capacitance (C) connected parallel with the resistor; hence thermal noise can be formulated as [17]:

$$\overline{v_n^{\,2}} = kT/C \quad (6)$$

So, from equation (6), we know that thermal noise of resistor in the same setup should be the same. Hence, we concluded that there exists noise phenomenon (excluding thermal noise) contributing to CNTs inherent noise. It is reported that 1/f noise (noise exists in many semi-conductor device) is one of the inherent noise in CNTs [18]. We believed that unexpected excessive noise in our f-CNTs sensor may also be 1/f noise. Further research on CNTs noise sources is undergoing in our group now.

V. CONCLUSION

We demonstrated here the great potential of turning chemically functionalized MWCNTs based sensors into ultra-low-powered, highly sensitive, reversible, and reproducible alcohol sensors. The sensors are proved to be operable at only ~0.006-0.04µW, which are 4 orders less power than the commercially available alcohol sensors. The sensitivity of the sensors has also noticeably increased after adding the functional group, i.e., COOH onto the nanotubes (from ~0.9% of a bare MWCNTs sensor to ~9.6% of an f-CNTs sensor with a dose of 100ppth alcohol vapor). Also, the reversibility of the sensors can be obtained easily by annealing them at ~100 to 250µA for 1 to 6 mins. Finally, the response is repeatable for vapor of all concentration as most of the fluctuations are within 10% of the average values. These positive results not only give us confidence to further our experiments on these COOH-MWCNTs as the sensing element for functional alcohol sensors, they also encourage us to work on matching other kinds of functionalized MWCNTs with different volatile organic compounds.

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