

# Comparison of Dynamic Response of Functionalized and Bare MWNT Sensors

Mengxing Ouyang<sup>1</sup>, Ka Wai Wong<sup>2</sup>, Wen J. Li<sup>1,\*</sup>, *Member, IEEE, Member, ASME*

<sup>1</sup>Centre for Micro and Nano Systems, Department of Mechanical and Automation Engineering,

<sup>2</sup>Department of Physics,

The Chinese University of Hong Kong, Shatin, N.T., Hong Kong SAR

\*[wen@mae.cuhk.edu.hk](mailto:wen@mae.cuhk.edu.hk)

**Abstract-** A resistive sensing device based on functionalized multi-walled carbon nanotubes (f-MWNTs) utilizing chemical oxidation method was fabricated successfully and proved sensitive to ethanol vapor. Dielectrophoresis (DEP) manipulation was used to achieve CNTs alignment between pairs of gold microelectrodes in fabricating the CNT sensing elements. I-V characteristics were tested to ensure that the sensors operate within the linear range, i.e., no over-heat ratio was induced onto the sensing elements during operation. Upon exposure to ethanol vapor, an increase of resistance was observed in both bare MWNTs and f-MWNTs sensors. However, compared to bare MWNTs, the f-MWNTs sensors proved to have lower power consumption (i.e., as low as nano-watt level), larger responsivity and faster time response. In addition, cycling responses of the sensors were evaluated and demonstrated to have good repeatability. Moreover, resistance of both sensors would drop under applied compressed air flow, which has been utilized to clear the residual ethanol and reset the sensors to their initial condition after each cycle of measurement.

## I. INTRODUCTION

Alcohol vapor has been one of the most extensively studied species among all gas sensing applications due to the demand of small and practical devices to detect alcohol for breathalyzers, or to identify industrial leakage in distribution lines [1]. Nowadays, metal oxide sensors (e.g., WO<sub>3</sub> [2], SnO<sub>2</sub> [3], and TiO<sub>2</sub> [4]), which exhibit the advantages of low cost, acceptable sensitivity and convenient form of resistive response [5], are becoming the most widely used ethanol sensors in the market. However, these kinds of sensors need to operate under elevated temperature (i.e., several hundred degree Celsius [6]) in order to achieve best performance [7], which result in the problem of high power consumption and long preheating time. Also, they suffer from the lack of high accuracy. For official use, i.e., ethanol concentration data acceptable in a litigation, therefore, metal oxide sensors are replaced by the fuel cell type alcohol sensors [8], which exhibit high accuracy, but have the drawbacks of high cost, and again, high power consumption. Other than these two types, porous silicon based gas sensors [9, 10] have also been reported by researchers for their large internal surface area, light emitting property, high chemical activity, as well as high sensitivity and efficiency in light absorption and sensing.

Within the last decade, carbon nanotube sensors have been receiving considerable attention with merits of high aspect ratio [11], minute size of the sensing element, and the

correspondingly small amount of source material required for a response [12]. Since the nanotube electronic property is a strong function of its atomic structure, mechanical deformations or chemical doping can induce great changes in conductance, which can be easily detected by electron current signals [13]. The capability of carbon nanotubes to serve as chemical sensing elements has been proved as early as 2000 [14]. Over the last decade, many research groups have been focusing on the gas adsorption mechanism of carbon nanotubes [15-18] as well as utilizing carbon nanotube based sensors to detect gases, such as CO<sub>2</sub> [19], NO<sub>2</sub> [20], and ammonia gas [21], etc. CNTs gas sensors have been proven to offer significant advantages over conventional electrical sensors in terms of sensitivity and room temperature operation [22].

Our group has been studying CNTs based ethanol vapor sensor since 2004 [23]. In our previous work, carbon nanotubes grafted with several kinds of functional groups have been proved sensitive towards ethanol molecules, and their potential to serve as ethanol vapor sensor have been demonstrated. The functional groups not only can enhance the sensibility of the ethanol vapor sensor, but also enable CNT sensors to achieve better selectivity towards different input measurands. In addition, we also evaluated different functional groups through both chemical and physical functionalization methods for the purpose of optimizing sensor performance. In this paper, we will present our latest progress on the ethanol vapor sensors based on f-MWNTs with COOH group grafted onto them by chemical oxidation. The sensor characterization and dynamic response were studied and compared to bare MWNTs sensors fabricated by the same process.

## II. FABRICATION OF ETHANOL SENSOR

### A. Sensor Fabrication & Experimental Setup

In our experiments, commercially available multi-walled carbon nanotubes (MWNTs) were employed and chemical oxidation method was used to graft functional group (e.g., -COOH) along the sidewall and the tube ends of the carbon nanotubes, which is illustrated in Fig. 1. The carbon nanotubes were first purified, and then sonicated. Finally, after the centrifugation, the functionalized MWNTs were collected, washed, and re-dispersed in solvent for use. The detail of functionalization process of carbon nanotubes are presented in

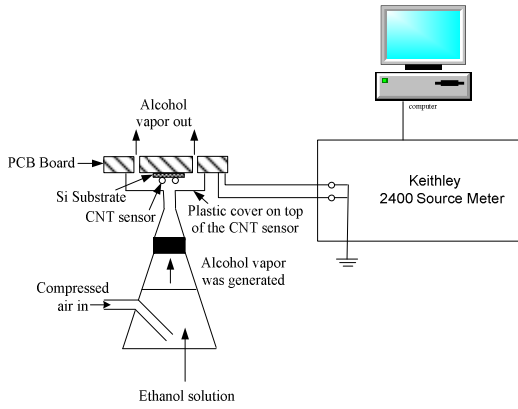


Fig. 1 Experimental setup to test the ethanol sensor.

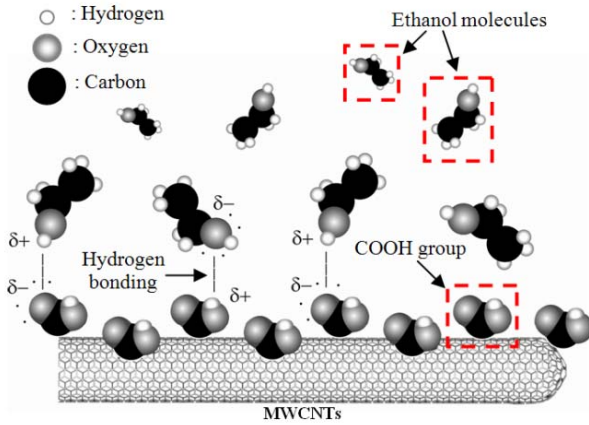


Fig. 2 Functionalized carbon nanotubes and the proposed sensing mechanism of ethanol sensor.

our earlier paper [14].

Dielectrophoresis (DEP) manipulation was used to form carbon nanotube linkage between microelectrodes [42], which were fabricated on Si substrate by photolithography procedure. During the DEP manipulation process, a droplet of f-MWNTs solution was transferred to the gap between a pair of Au microelectrodes, which were excited by an AC bias voltage (8V peak-peak at 1MHz). After the evaporation of solvent, f-MWNTs connections were made between the two electrode tips. Typically, the two-probe room temperature resistance of the f-MWNTs based devices range from several tens of kilo-Ohms to several hundreds of kilo-Ohms, depending on the concentration and volume of the solution droplet. Bare MWNTs sensing elements were also fabricated using the exact same process as described above.

Then, a sensor chip with CNTs connection between microelectrodes was fixed and wire-bonded to a printed circuit board (PCB) for measurements. A commercial source meter (Keithley 2400 Source Meter) was employed to measure and collect the electrical signals of the CNTs sensors. The experimental setup is shown in Fig.1.

### B. Sensing Mechanism

Once encountering the OH group of ethanol molecules in the ambient environment, the -COOH group attached to the carbon nanotubes would interact with the OH group through hydrogen

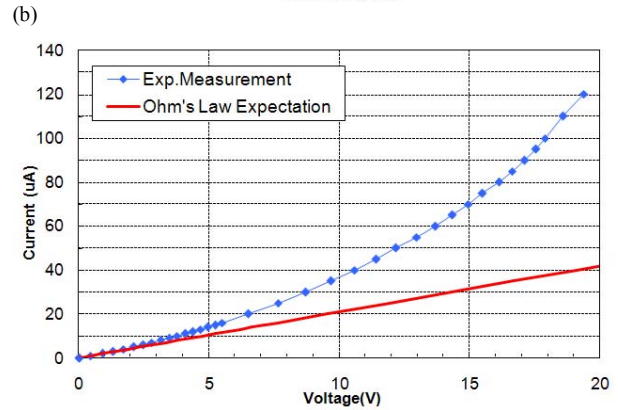
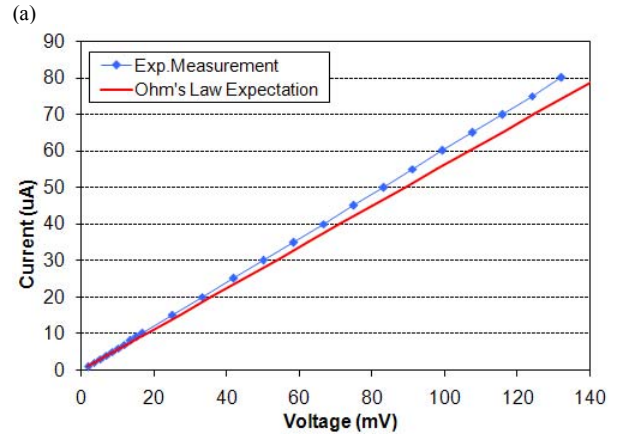
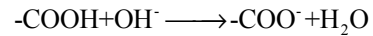


Fig. 3 I-V curve of (a) MWNT sensor (b) f-MWNT sensor.

bonds, which further leads to the resistance change of the ethanol vapor sensors. Fig. 2 illustrates the proposed mechanism of f-MWNT based ethanol vapor sensors. The main chemical reaction is given below:



We note here that the whole process is reversible if the ethanol molecules attached to the sensor surface are eliminated. Details of an annealing method to eliminate the attached ethanol molecules will be revealed in a later section.

## III. COMPARISON BETWEEN F-MWNTS AND MWNTS

### A. I-V Characteristics

During the experiments, the I-V characteristics of MWNTs and f-MWNTs sensors were first investigated. Fig. 3 shows the typical I-V curves of the MWNTs and f-MWNTs sensing elements made in our laboratory. The two-probe room resistance for both types of sensors ranges from several kilo-Ohms to several hundred kilo-Ohms typically. The measured data were compared to the Ohm's law expectation, which indicates the ideal sensor behavior when no self-heating effect occurs. As shown in the figure, both MWNTs and f-MWNTs exhibited linear current-voltage relationship at first, and then showed self-heating effect starting at around 10  $\mu\text{A}$ . Then, in the nonlinear region, the resistance drops as temperature rises. The behavior of sensors in the nonlinear region under relatively large current implied their negative Temperature Coefficient of Resistance (TCR) characteristics.

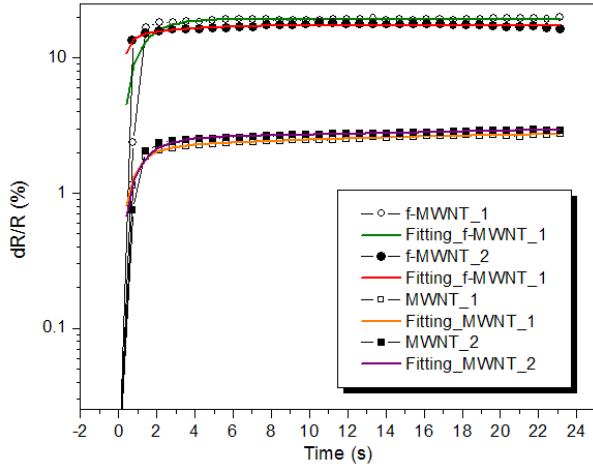


Fig. 4 Time response of bare MWNTs and f-MWNTs sensors.

In our applications, the activation current was controlled to enable the ethanol sensors to work within the linear range and avoid self-heating effect. Under this circumstance, both bare MWNT and f-MWNT ethanol sensors operate under power consumptions around nano-watt level (i.e.,  $\sim 0.05\mu\text{A}$  at  $\sim 0.02\text{V}$ ). This ultra-low power consumption property enables the sensors to pick up the physical parameters with minimal thermal disturbance [24], which is indispensable for sensing true measurands in micro scale world and desirable for future gas sensing applications.

### B. Dynamic Response

Furthermore, we compared the response of the two kinds of ethanol sensors. One sensor of each type was tested: the two-probe room temperature resistance of the bare MWNTs and f-MWNTs sensors were  $\sim 1.7$  kilo-Ohms and  $\sim 430$  kilo-Ohms, respectively. Considering the detecting range and measuring precision of the source meter, as well as the constraint of controlling a sensor within its linear resistance region, the operating current used in the experiment were  $\sim 10\mu\text{A}$  for the MWNTs sensor and  $0.05\mu\text{A}$  for the f-MWNTs sensor. Hence, the power consumption of the bare MWNTs and f-MWNTs were  $170$  nW and  $1.08$  nW, respectively.

Upon exposure to the ethanol vapor, a sharp increase of resistance was observed almost instantaneously, which all owed us to evaluate the time response of bare MWNTs and f-MWNTs sensors (see Fig. 4). While exposing to  $25\text{ppH}$  ethanol concentration for the same duration, f-MWNT showed a response of  $\sim 20\%$  resistance increase, while the resistance of MWNTs only increased by  $\sim 3\%$ . For each sensor, two consecutive experiments were conducted to ensure repeatability. Also, as shown in Fig. 4, the response matched well with first-order exponential decay functions.

One of the essential parameters to evaluate the sensor performance is time constant ( $\tau_{60}$ ), which is defined as the time it takes the system's step response to reach approximately 63% of its final (asymptotic) value towards detecting an input. Applying this definition, the time constant for bare MWNTs and f-MWNT sensors, which were obtained from the response curve, are  $18.4\text{s}$  and  $1.3\text{s}$ , respectively. However, these time constants were obtained based on two sensors tested thus far

TABLE I COMPARISON BETWEEN BARE MWNTS AND F-MWNTS

	Resistance (kilo-Ohms)	Power Consumption (nW)	Response ( $\Delta R/R$ )	Time Constant ( $\tau_{60}$ , s)
MWNT	$\sim 1.7$	$\sim 170$	$\sim 3\%$	$\sim 18.4$
f-MWNT	$\sim 430$	$\sim 1.08$	$\sim 20\%$	$\sim 1.3$

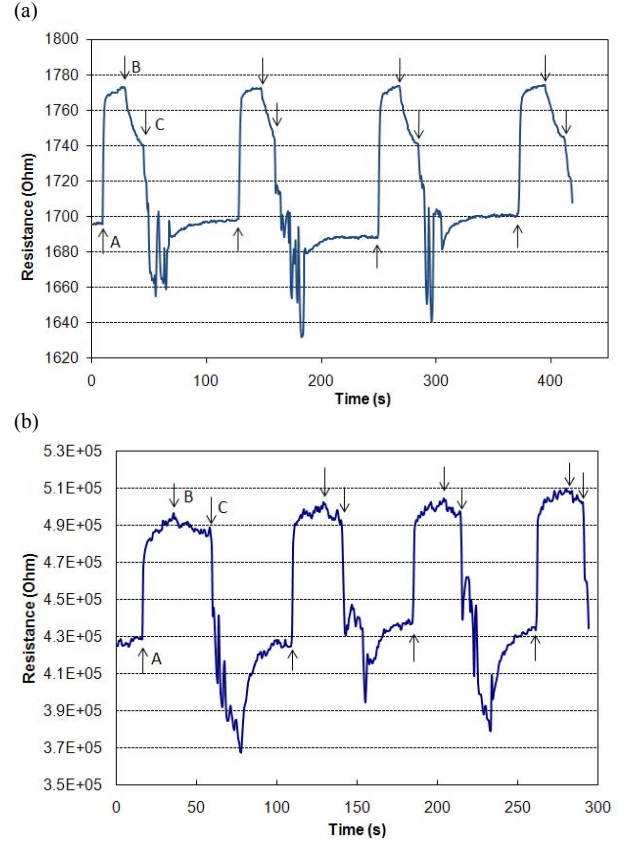


Fig. 5 Cycling response of (a) MWNTs sensor (b) f-MWNTs sensor.

(one MWNTs and one f-MWNTs). More detailed experiments are underway in our lab to validate these time constants.

The comparison results between MWNTs and f-MWNTs are summarized in Table 1. The COOH group did not only helped MWNT obtain better responsivity towards ethanol vapor, but also enable the sensor to exhibit faster response under lower power consumption.

### C. Cycling Response

In order to evaluate the repeatability of the ethanol sensors, four cycles of consecutive measurements were carried out. The results for bare MWNTs and f-MWNTs are demonstrated in Fig. 5 (a) and (b), respectively. In each measuring cycle, the sensor was exposed to ethanol vapor for approximately 20 seconds, which started at point A and ended at point B. During this period, sensor responded with a quick increase of resistance and then reached equilibrium in a few seconds. Once the ethanol vapor was withdrawn, the resistance would drop gradually towards its original resistance. However, this naturally recovery process takes too long (i.e., could be in the order of hours) and may not achieve the original resistance eventually. Therefore, it is infeasible for commercial applications. Moreover, the residual ethanol vapor could jeopardize the sensor responsivity if additional vapor detection

is required, i.e., the responsivity tends to decline severely even though if the same concentration of ethanol vapor is provided as input. For the purpose of reversible detection, we utilized air flow to clean up the residual ethanol molecules attached along the nanotube. In Fig. 5, point C stands for the moment when compressed air was blown onto the sensor surface. As shown, the air flow immediately led to a dramatic decrease of the sensor resistance. The fluctuation in the figures is caused by the movement of the compressed air tube, which is controllable and would not affect sensor performance. However, once the air-flow was removed, the sensor resistance would increase gradually to its static value.

Besides, other experiments were also conducted to study the sensor behavior towards air flow. On the contrary to what we have observed upon exposure to ethanol vapors, both bare MWNTs and f-MWNTs showed decrease in resistance due to air flow, which is in accordance with the results in Fig. 5.

To ensure that the sensors have been reset to their initial condition, a higher current, i.e., 100  $\mu$ A to 200 $\mu$ A, was applied to the sensors for around 5 minutes other than air-flow annealing. The purpose is also to get rid of the residual ethanol molecules. Despite of the existence of the resistance drift, the sensors usually recover to almost the same level as their original resistance value.

#### IV. CONCLUSION

In order to evaluate the dynamic performance of functionalized carbon nanotube sensors, a novel ethanol vapor sensor utilizing COOH group functionalized MWNTs as sensing elements was fabricated by DEP manipulation. Experiments were carried out to compare these f-MWNTs sensors with bare MWNT sensors. Both sensors showed similar current-voltage behavior, negative TCR, and a rising of resistance towards ethanol vapor. Operating within linear resistance range, f-MWNTs sensors proved larger responsivity under the same ethanol concentration due to the existence of COOH group, which chemically interact with ethanol molecules. Moreover, the f-MWNTs sensors exhibit the advantage of shorter response time (smaller time constant) compared to the bare MWNT sensors. Compressed air-blowing and relatively high current heating were introduced in the recovery process and ensured the reliability of sensors. To sum up, with merits of ultra-low power consumption, high responsivity, fast response, and no heating elements needed during detection, functionalized MWNTs sensors are desirable for future gas sensing applications.

#### ACKNOWLEDGMENT

This project is funded by the Hong Kong Research Grants Council (Project code: 413906).

#### REFERENCES

- [1] Mandy L. Y. Sin, Gary C. T. Chow, Gary M. K. Wong, Wen J. Li, Philip H. W. Leong, and K. W. Wong, "Ultra-low-power alcohol vapor sensors using chemically functionalized multi-walled carbon nanotubes", *IEEE Trans. on Nanotechnology*, accepted, 2007.
- [2] T. Champaiboon, S. Ruangsuttinarupap, and S. Supothina, "Efficiency enhancement of a tungsten oxide alcohol sensor", *4<sup>th</sup> Thailand Mater. Sci. and Tech. Conf.* 2006
- [3] Hae-Won Cheong and Man-Jong Lee, "Sensing characteristics and surface reaction mechanism of alcohol sensors based on doped SnO<sub>2</sub>", *J. of Ceramic Proc. Research*, Vol. 7, No. 3, pp. 183-191, 2006.
- [4] S. Mishra, C. Ghanshyam, N. Ram, S. Singh, R. P. Bajpai, and R. K. Bedi, "Alcohol sensing of tin oxide thin film prepared by sol-gel process", *Bull. Mater. Sci.*, Vol. 25, No. 3, pp. 231-234, 2002.
- [5] S. Kim, "CNT sensors for detecting gases with low adsorption energy by ionization", *Sensors*, Vol. 6, pp. 503-513, 2006.
- [6] M. M Zhang, and G. S. Jiang, "Gas sensing properties of Co<sub>3</sub>O<sub>4</sub>-loaded SnO<sub>2</sub> to ethanol and acetone", *Chin. J. Chem. Phys.*, Vol. 20, pp. 315-318, 2007.
- [7] G. Sberveglieri, E. Comini, G. Faglia, M. Z. Atashbar, and W. Wlodarski, "Titanium dioxide thin films prepared for alcohol microsensor applications", *Sensors and Actuators B*, Vol. 66, pp. 194-141, 2000.
- [8] K. C. Kim, S. M. Cho, and H. G. Choi, "Detection of ethanol gas concentration by fuel cell sensors fabricated using a solid polymer electrolyte", *Sensors and Actuators B*, Vol. 67, pp. 194-198, 2000.
- [9] S. J. Kim, B. H. Jeon, K. S. Choi, and N. K. Min, "Capacitive porous silicon sensors for measurement of low alcohol gas concentration at room temperature", *J. Solid State Electrochem*, Vol. 4, pp. 363-366, 2000.
- [10] Y. C. Bow, W. M. Kwok, and M. C. Poon, "Porous silicon ethanol vapor sensor", *IEEE Electron Devices Meeting*, pp. 13-16, 1996.
- [11] S. Reich, C. Thomsen, and J. Maultzsch, *Carbon nanotubes, basic concepts and physical properties*. Berlin: WILEY-VCH, 2004, pp. 3-30, 60-65.
- [12] Ray H. Baughman, Anvar A. Zakhidov, and Walt A. de Heer, "Carbon Nanotubes—the route toward applications", *Science*, Vol. 297, pp. 787-792, 2002.
- [13] S. Peng, J. O'Keeffe, C. Wei, and K. Cho, "Carbon nanotube chemical and mechanical sensors", *3<sup>rd</sup> Int. Workshop on Structural Health Monitoring*, 2004.
- [14] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, and H. Dai, "Nanotube Molecular Wires as chemical sensors," *Science*, Vol. 287, pp. 622-625, 2000.
- [15] Meng-Hung Tsai, Hong-Ming Lin, Wen-Li Tsai, and Yeukuang Hwu, "Examined the gas absorption properties of single wall carbon nanotube bundles by X-ray absorption techniques", *Rev. Adv. Mater. Sci.*, Vol. 5, pp. 302-305, 2003.
- [16] Wei Shi, and J. Karl Johnson, "Gas adsorption on heterogeneous single-walled carbon nanotube bundles", *Phys. Rev. Lett.*, Vol 91, pp. 015504 1-4, 2003.
- [17] A. Fujiwara, K. Ishii, H. Suematsu, H. Kataura, Y. Maniwa, and S. Suzuki *et al.*, "Gas adsorption in the inside and outside of single-walled carbon nanotubes", *Chem. Phys. Lett.* Vol. 336, pp. 205-211, 2001.
- [18] O. K. Varghese, P. D. Kichambre, D. Gong, K. G. Ong, E. C. Dickey, and C. A. Grimes, "Gas sensing characteristics of multi-wall carbon nanotubes", *Sensors and Actuators B*, Vol. 81, pp. 32-41, 2001.
- [19] Keat Ghee Ong, Kefeng Zeng, and Craig A. Grimes, "A Wireless, passive carbon nanotube-based gas sensor", *IEEE Sensors Journal*, Vol. 2, pp. 82-88, 2002.
- [20] Kay Hyeok An, Seung Yol Jeong, Ha Ryong Hwang, and Young Hee Lee, "Enhanced sensitivity of a gas sensor incorporating single-walled carbon nanotube-polyppyrrrole nanocomposites", *Adv. Mater.* Vol. 16, pp. 1005-1009, 2004.
- [21] Junya Suehiro, Guangbin Zhou and Masanori Hara, "Fabrication of a carbon nanotube-based gas sensor using dielectrophoresis and its application for ammonia detection by impedance spectroscopy", *J. Phys. D: Appl. Phys.*, Vol. 36, pp. L109-L114, 2003.
- [22] Y. W. Chang, J. S. Oh, S. H. Yoo, H. H. Choi, and K. H. Yoo, "Electrically refreshable carbon-nanotube-based gas sensors", *Nanotechnology*, Vol. 18, pp. 435504, 2007.
- [23] Mandy L. Y. Sin, Gary C. T. Chow, Carmen K. M. Fung, Wen J. Li, Philip H. W. Leong, K. W. Wong, and Terry Lee, "Ultra-low-power alcohol vapor sensors based on multi-walled carbon nanotubes", *IEEE Int. Conf. on Nano/Micro Engineered and Molecular Systems*, pp.1198-1202, Jan. 18-21, 2006.
- [24] Mandy L. Y. Sin, Gary C. T. Chow, M. K. Wong, Wen J. Li, Philip H. W. Leong, K. W. Wong, and Terry Lee, "Chemically functionalized multi-walled carbon nanotube sensors for ultra-low-power alcohol vapor detection", *IEEE Int. Conf. on Nanotechnology*, Vol. 2, pp.461-464, 2006.