

## Gas Sensing Performance of Composite Materials Using Conducting Polymer/Single-Walled Carbon Nanotubes

Hyang Hee Choi<sup>1</sup>, Junmin Lee<sup>1</sup>, Ki-Young Dong<sup>2</sup>, Byeong-Kwon Ju<sup>2</sup>, and Wooyoung Lee<sup>\*,1</sup>

<sup>1</sup>Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea

<sup>2</sup>Display and Nanosystem Laboratory, College of Engineering, Korea University, Seoul 136-713, Korea

Received April 1, 2011; Revised August 26, 2011; Accepted August 30, 2011

**Abstract:** We report the fabrication of a novel gas sensor that utilizes electrical resistance changes in electrically conductive polyaniline (PANI) and single-walled carbon nanotube (SWNT) composite materials and its sensing property when NH<sub>3</sub> and CO gases co-existed. In addition, we investigated the concentration dependence of electrical properties of the PANI/SWNT composite material at room temperature using real-time monitoring. To improve the gas sensor properties, we deposited PANI using a drop-casting method to wrap the PANI surrounding the SWNT. The PANI/SWNT composite material sensors showed a faster response to NH<sub>3</sub> gas than CO gas. The CO gas increased the composite conductance, while the NH<sub>3</sub> gas had the opposite effect.

**Keywords:** gas sensors, electrical resistance, conducting polymer, single-walled carbon nanotubes (SWNTs), unsafe gases.

### Introduction

Environmentally unsafe gases are known to be directly harmful to humans. The main hazardous gases include carbon monoxide, carbon hybrids, nitrogen oxides, sulfur hydrogen, and volatile organic compounds. In order to monitor air pollutants, high performance sensors that can identify and measure gaseous and vapor species are required. In addition, the use of an electronic method for measuring gas is highly desirable for the mobile and *in situ* monitoring. Several materials have been utilized as gas sensors, including metal oxides, nanowires, organic semiconductors, and carbon nanotubes (CNTs).<sup>1</sup> Studies have also been made on sensing materials whose properties allow for fast response and high sensitivity to specific gases. Conjugated polymers have long been considered, especially as gas sensing materials, although these materials are limited by electrostatic/dielectric interferences and fragile organic metal interfaces. Polyaniline (PANI) is one of the conducting polymers for gas sensing applications due to its ease of preparation, relatively high electrical/environmental stability and low resistivity.<sup>2,3</sup> Single-walled carbon nanotubes (SWNTs) have also received considerable attention as chemical sensor materials because of their high sensitivity and real-time detection capabilities. The cylindrical shapes and high aspect ratios of SWNTs provide a large surface to volume characteristic, which offers ideal and selective physico-chemical adsorption

for specific gas. Despite their high sensitivity, the applications of these materials have been restricted due to their poor selectivity for the detection of coexisting NH<sub>3</sub> and CO gases.

Recently, gas sensors based on conducting polymer/SWNTs systems have been reported. CNT-based gas sensors have been studied based on the observation that their electrical properties change with gas adsorption.<sup>4</sup> Although the behaviors of these sensors with many noxious gases including NO<sub>x</sub>,<sup>5</sup> CO,<sup>6</sup> NH<sub>3</sub>,<sup>7</sup> and volatile organic compounds (VOC) have been reported,<sup>8</sup> of the detection of coexisting NH<sub>3</sub> and CO gases has not been reported. For the commercialization of gas sensors using CNTs as sensing materials, the relative sensitivity to each gas molecule should be analyzed in a coexisting gas environment. In fact, sensing coexisting gas molecules is important in environmental monitoring, control of chemical and agricultural processes, and biological and medical applications.

Carbon monoxide is a significantly toxic gas and has neither odor nor color. It is the most common cause of fatal poisoning in many countries. Symptoms of mild poisoning include headaches and dizziness at concentrations less than 100 ppm.<sup>9,10</sup> In addition, ammonia is classified as toxic and harmful to the environment. NH<sub>3</sub> is a very odiferous gas with a characteristic pungent smell. In addition, NH<sub>3</sub> is flammable and can form explosive mixtures with air.<sup>11</sup> The detections of NH<sub>3</sub> and CO gases have been reported by Santucci *et al.* and Kong *et al.*, respectively.<sup>12,13</sup> In fact, CO gas is difficult to measure at room temperature using SWNTs. In this work,

\*Corresponding Author. E-mail: wooyoung@yonsei.ac.kr

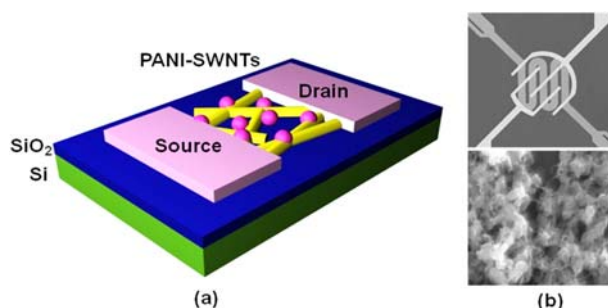
we have investigated the detection of the  $\text{NH}_3$  and CO gases using PANI/SWNTs composite at room temperature. The PANI/SWNTs composite material sensors showed a faster response to  $\text{NH}_3$  gas than CO gas. The CO gas increased the conductance of the composite, while  $\text{NH}_3$  gas showed an opposite response. CO gas molecules are adsorbed chemically onto the surfaces of the PANI/SWNTs and work as hole donors, while the  $\text{NH}_3$  molecules are physically adsorbed and work as hole acceptors.<sup>14,15</sup> In addition, we have studied the characteristics of PANI/SWNTs composite sensors to selectively detect gases under a coexisting atmosphere in terms of gas sensitivity and selectivity. For further practical application, we have also analyzed the detections of  $\text{NH}_3$  and CO gases individually and in the coexisting state using PANI/SWNTs composite gas sensors.

## Experimental

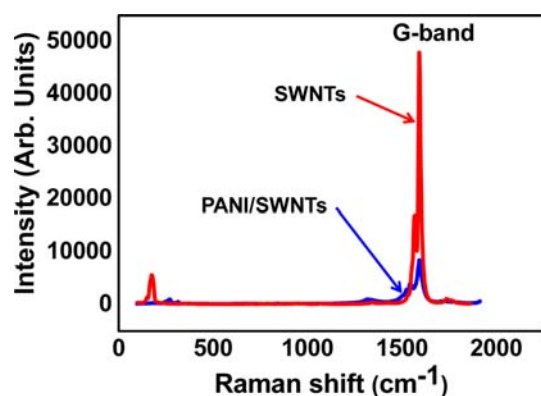
All chemicals were of analytical reagent grade. Purified arc discharge nanotubes with 70%-90% purity were purchased from Iljin Nanotech Co., Ltd. Sulfuric, hydrochloric, and nitric acids were purchased from Sigma-Aldrich, and sodium dodecyl sulfate (SDS) surfactant was purchased from Samchun Chemistry in Korea. The purified SWNTs were dissolved in 0.2 wt% SDS surfactant using deionized water. Dispersion of SWNTs was carried out in a bath-sonicator for 4 h, and vacuum filtration was performed with Teflon filters (Millipore, pore size 20  $\mu\text{m}$ ). After filtration, the filtered film was rinsed with deionized water for several minutes to remove SDS surfactant.<sup>16</sup> PANI was synthesized through the chemical oxidative polymerization of aniline in an aqueous acidic media containing 1.33 M HCl using double distilled water. Conducting HCl-doped PANI was dissolved in *N,N'*-dimethyl formamide (DMF) under an inert atmosphere. The mixed solution of SWNTs and PANI was stirred continuously for 24 h at room temperature. Then the PANI/SWNTs films were prepared by drop casting the solution on a substrate. Reflecting mode field-emission scanning electron microscopy (FE-SEM, Jeol Model JSM-6500F) was used to measure the film thickness and morphology. The flow rate of air and the concentrations of CO,  $\text{NH}_3$ , and mixed gas were controlled by pneumatic mass flow controllers (MFCs). The resistance change value was measured and stored by a source meter (Keithley 2400) and Labview (National Instrument Corp., Austin, TX) software, respectively. Gas sensing experiments were performed in a vacuum chamber (100 L) with a vacuum pump outlet and a syringe port. During the experiments, the gas sensor was placed in a sealed chamber at a vacuum pressure of  $2 \times 10^{-3}$  Torr. Sensing devices were fabricated by evaporating a 3 nm Ti/50 nm Au electrode onto a silicon substrate using a thermal evaporator.<sup>17</sup> The PANI/SWNTs composite materials were characterized using a semiconductor parameter analyzer and MFCs located in the gas chamber.

## Results and Discussion

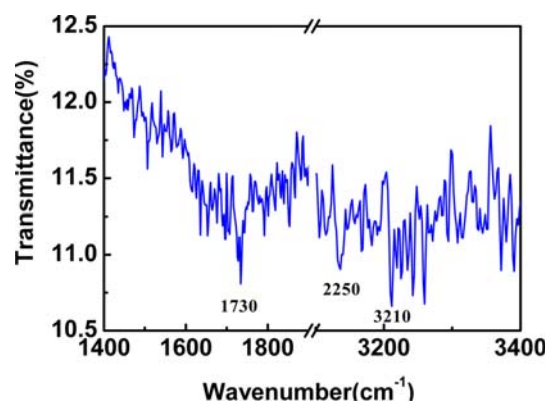
Figure 1 illustrates the schematics of the random adsorption of PANI molecules onto SWNTs. The expanded view in Figure 1 shows a typical FE-SEM image of the PANI/SWNTs composite materials, illustrating a homogeneous coating indicative of well-dispersed SWNTs. It can also be seen that the composite film displays a new interwoven fibrous structure with a diameter of 1-10 nm. This new network may give rise to conductive pathways and lead to high conductivity. It is well known that both PANI and SWNTs exhibit *p*-type semiconductor characteristics. Thus, these materials exhibit reduced charge carrier concentrations and decreases in conductance when they are exposed to a hole accept gas molecule, such as  $\text{NH}_3$ . A resistance decrease of a PANI film was detected when it exposed to CO.<sup>14</sup> From the previous work, we can also speculate sensing mechanism.<sup>18</sup> The hole at the carbon atom (in CO) responds to the amine nitrogen (-NH-) in the PANI, so that the positive charge is transferred from the carbon to amine nitrogen, and therefore an increase in conductivity. The similar phenomena were also observed in the interaction between chlorinated hydrocarbon and PANI.<sup>19</sup> The Raman spectrum of pristine SWNTs in Figure 2 displays two strong bands; the so-called radial breathing mode (*ca.* 209  $\text{cm}^{-1}$ , RBM) and the tangential mode (*ca.* 1590  $\text{cm}^{-1}$ , G-band). The multiple peaks observed in the RBM are ascribed to the distribution of diameters in the SWNTs sample. In the spectra shown in Figure 3, infrared absorption peaks at 3210, 2250, and 1730  $\text{cm}^{-1}$  were probably assigned to N-H, C=O, and C-H or C=O, respectively, covalently attached to the C atoms on the SWNTs ends and/or sidewalls. The conductance response to CO shown in Figure 4(b) illustrates different behaviors from that of  $\text{NH}_3$  in Figure 4(a). Since the pristine SWNT-based sensor was insensitive to CO gas due to the low affinity to pristine SWNTs, we considered that PANI was responsible for the observed increase in conductance under CO gas. As previously mentioned, the CO gas sensing mechanisms for



**Figure 1.** (a) Schematic diagrams of the random adsorption of gas molecules onto SWNTs. Ohmic characteristics were measured using Ti/Au metal electrodes at the source and drain. (b) The device image (upper image) and FE-SEM image of PANI/SWNTs films prepared on a Si substrate (lower image).

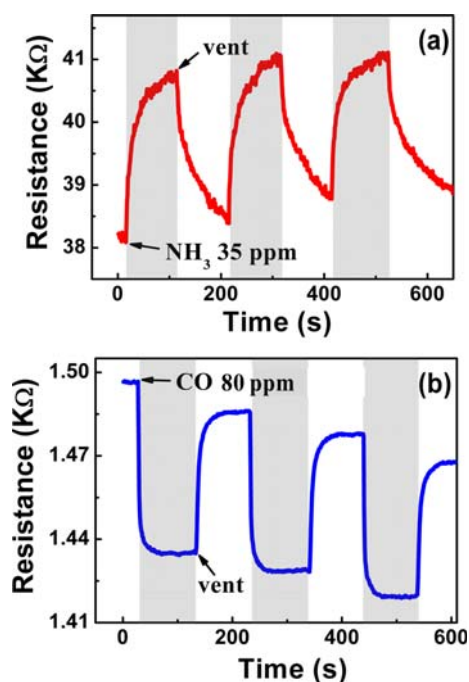


**Figure 2.** Raman spectra (514 nm excitation) of SWNTs. Purified SWNTs (Red line) and PANI/SWNTs (Blue line).

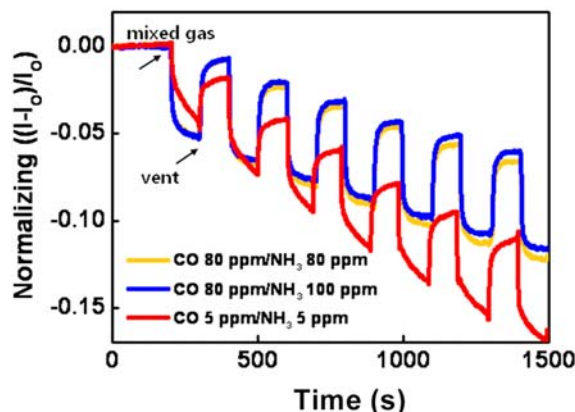


**Figure 3.** FTIR spectra of PANI/SWNTs composite materials.

many conductive polymers are not fully understood. Carboxylic acid group and defect sites may be formed on SWNT sidewalls as a result of purification steps, and interaction with CO molecules likely occurred.<sup>20</sup> Consequently, the COOH functionality and defect sites may play a key role in CO detection, resulting in a decrease in the electrical resistance of CNTs, despite the interaction with the hole-donating gas. The CO sensing mechanism of PANI is not yet clear, but two plausible explanations have been proposed. One is that the CO ( $\text{CO}^+$ ) can naturally interact with undoped nitrogen atoms in the PANI chains to produce a polaron ( $-\text{NH}^{\cdot+}$ ) such that the conversion induces a higher density of charge carriers, thus increasing the conductance. Another possibility is that oxidation occurs at the grain surfaces in the presence of CO, such that the barrier height and depletion length between grains are reduced, this increasing the conductance. In another test, the real-time conductance response of the PANI/SWNTs composite sensor to coexisting  $\text{NH}_3$  and CO gases is presented in Figure 5. As shown in Figure 4(a), (b), and Figure 5, the relative resistance change  $\Delta R/R_0 = (R_g - R_0)/R_0$  was plotted as a function of gas concentrations, where  $R_g$  is the resistance after the third recovery and  $R_0$  is the resistance after the fourth gas exposure. The



**Figure 4.** Electrical resistance changes in the sensor as a function of time for five cycles at room temperature with (a) 35 ppm  $\text{NH}_3$  and (b) 80 ppm CO.



**Figure 5.** Electrical resistance changes in the sensor as a function of time for six cycles at room temperature with various concentrations of  $\text{NH}_3$  and CO gas mixture.

PANI/SWNTs composite sensor exhibited linear responses to all gases. To this end, the conductance of the PANI/SWNTs composite sensor increases in the presence of coexisting CO and  $\text{NH}_3$  gases, such that it is difficult to distinguish between CO and  $\text{NH}_3$  by measuring the conductance change. However, since we presume the absorption of  $\text{NH}_3$  is much faster than that of CO, exposures to CO and  $\text{NH}_3$  gases yield different response patterns. Firstly absorbed  $\text{NH}_3$  gas dominantly reacts with the composite materials, and followed reaction with CO gas cannot probably function properly in the total reaction. Consequently, the sensors may not be able

to identify the presence of CO gas and the response tendency of NH<sub>3</sub> gas is only observed. Based on these results, CO and NH<sub>3</sub> will be distinguished using the PANI/SWNTs composite sensor for further studies.

## Conclusions

SWNT-based sensors were used to detect resistance change when exposed to two types of gases. When the sensor was individually exposed to NH<sub>3</sub> and CO, the sensor resistance increased and decreased, respectively. However, in the case of coexisting gases, the resistance increased due to the different absorbability of NH<sub>3</sub> and CO with the surface of the PANI/SWNTs composite. Since the absorption response of NH<sub>3</sub> might be faster than that of CO, the resistance increased over the initial value. Consequently, the PANI/SWNTs composite showed the higher sensitivity to NH<sub>3</sub> than to the CO later adsorbed. The HCl-doped PANI on SWNTs produces strong interfacial bindings with the polymer matrix because the mobility of the polymer chains and degradation product are reduced. This gas sensor may be used in many areas, such as toxic gas detection, chemical leak detection, and in military, industry and medical applications. These possibilities are currently under further investigation.

**Acknowledgments.** This work was supported by the Priority Research Centers Program (2010-0028296) and the Basic Research Program grant (2010-0027687) through the National Research Foundation of Korea (NRF).

## References

- (1) A. Maiti, in *Computational Methods for Sensor Material Selection*, Springer, New York, 2010, Part 1, p 47.
- (2) K. Ramanathan, M. A. Bangar, M. H. Yun, W. F. Chen, A. Mulchandani, and N. V. Myung, *Nano Lett.*, **4**, 1237 (2004).
- (3) J. Wang, S. Chan, R. R. Carlson, Y. Luo, G. L. Ge, R. S. Ries, J. R. Heath, and H. R. Tseng, *Nano Lett.*, **4**, 1693 (2004).
- (4) B. Mahar, C. Laslau, R. Yip, and Y. Sun, *IEEE Sens. J.*, **7**, 266 (2007).
- (5) J. Kong, M. G. Chapline, and H. J. Dai, *Adv. Mater.*, **13**, 1384 (2001).
- (6) K. G. Ong, K. Zeng, and C. A. Grimes, *IEEE Sens. J.*, **2**, 88 (2002).
- (7) L. Valentini, C. Cantalini, I. Armentano, J. M. Kenny, L. Lozzi, and S. Santucci, *J. Vac. Sci. Technol. B*, **21**, 1996 (2003).
- (8) J. Li, Y. J. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, *Nano Lett.*, **3**, 929 (2003).
- (9) S. T. Omaye, *Toxicology*, **180**, 139 (2002).
- (10) G. P. Roberts, H. Youn, and R. L. Kerby, *Microbiol. Mol. Biol. Rev.*, **68**, 453 (2004).
- (11) N. H. Quang, M. V. Trinh, B. H. Lee, and J. S. Huh, *Sens. Actuators B: Chem.*, **113**, 341 (2006).
- (12) S. Santucci, S. Picozzi, F. Di Gregorio, L. Lozzi, C. Cantalini, L. Valentini, J. M. Kenny, and B. Delley, *J. Chem. Phys.*, **119**, 10904 (2003).
- (13) J. Kong, N. R. Franklin, C. W. Zhou, M. G. Chapline, S. Peng, K. J. Cho, and H. J. Dai, *Science*, **287**, 622 (2000).
- (14) J. Zhao, A. Buldum, J. Han, and P. Lu, *Nanotechnology*, **13**, 195 (2002).
- (15) H. Bai and G. Shi, *Sensors*, **7**, 267 (2007).
- (16) M. S. Strano, V. C. Moore, M. K. Miller, M. J. Allen, E. H. Haroz, C. Kittrell, R. H. Hauge, and R. E. Smalley, *J. Nanosci. Nanotech.*, **3**, 81 (2003).
- (17) Y. W. Chang, J. S. Oh, S. H. Yoo, H. H. Choi, and K. H. Yoo, *Nanotechnology*, **18**, 435504 (2007).
- (18) S. Watcharaphalakorn, L. Ruangchuay, D. Chotpattahanont, A. Sirivat, and J. Schwank, *Polym. Int.*, **54**, 1126 (2005).
- (19) G. Anitha and E. Subramanian, *Sens. Actuators B: Chem.*, **107**, 605 (2005).
- (20) D. Fu, H. Lim, Y. Shi, X. Dong, S. G. Mhaisalkar, Y. Chen, S. Moochhala, and L. Li, *J. Phys. Chem. C*, **112**, 650 (2008).