Sensors and Actuators B 209 (2015) 444–448

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Nano-composite sensors composed of single-walled carbon nanotubes and polyaniline for the detection of a nerve agent simulant gas

Ran Yoo[a], Jeongmin Kim[a], Min-Jung Song[a], Wooyoung Lee[a,*], Jin Seo Noh[b,*]

[a] Department of Materials Science and Engineering,Yonsei University, 134 Shinchon, Seoul 120-749, Republic of Korea
[b] Departmemt of Nano-Physics, Gachon University, 1342 Seongnamdaero, Seongnam-si, Gyeonggi-do, Republic of Korea

ARTICLE INFO

Article history:
Received 12 July 2014
Received in revised form
18 November 2014
Accepted 19 November 2014
Available online 4 December 2014

Keywords:
SWCNTs
Polyaniline
DMMP
Gas sensor

ABSTRACT

This paper reports the response behavior at room temperature of a composite sensor composed of single-walled nanotubes (SWCNTs) and polyaniline, to the nerve agent simulant gas dimethyl-methyl-phosphonate (DMMP), a typical Sarin simulant. The SWCNT–polyaniline composite was synthesized to obtain high-quality composites with good uniformity. The composites were drop-cast onto an oxidized Si substrate patterned with Pd electrodes. SWCNT–polyaniline composite sensors exhibited clear, sharp response curves for DMMP in air at room temperature, even at minuscule concentrations. The response and response time were 27.1% and 5.5 s, respectively, at 10 ppm DMMP, representing a significant improvement over the pure SWCNT network sensors previously reported. These results indicate that SWCNT–polyaniline composite sensors can be ideal DMMP sensors, operating at room temperature with high response, fast response time, and excellent reproducibility.

1. Introduction

Sarin is one of the strongest nerve gas agents available. It has often been used for chemical warfare, producing disastrous effects within seconds after inhalation. Owing to Sarin's rapid action and deadliness, the development of a fast, accurate gas detection method is paramount [1,2]. Dimethyl-methyl-phosphonate (DMMP) is a typical simulant of Sarin that many researchers use in Sarin gas-related experiments. Various DMMP gas detection methods have been developed, including methods using semiconducting metal oxide (SMO) sensors [3,4], surface acoustic wave sensors [5–9], and micro-cantilever sensors [10,11]. Of the aforementioned sensors, SMO sensors have already been commercialized owing to their advantageously high response and short response time; however, they require a high operation temperature, preventing their widespread use. To address this issue, carbon nanotube (CNT)-based sensors have recently been investigated. CNTs have intriguing properties, including chemical stability and large surface area [12–15]. CNT-based sensors in general are highly sensitive, respond quickly, and operate at room temperature [16–18].

In previous DMMP detection research, pure SWCNT network sensors with palladium (Pd) electrodes were fabricated and reported [18]. Although pure SWCNT-based sensors are easy to fabricate and can operate at room temperature, their low response and relatively long response time are unresolved issues. Similar result was reported by Wang et al., who obtained a response of 2% at a 10 ppm DMMP using SWCNTs [19]. Novak et al. fabricated SWCNT-based field effect transistors (FETs) and demonstrated the rapid detection of DMMP using them, but a certain amount of gate bias was required to refresh the FET to the original state [20,21]. The same research group also utilized SWCNT-based capacitors to swiftly detect a small amount of DMMP [22]. In another research, Cho et al. achieved a low detection limit of 5 ppb and a short response time of <1 s using polyaniline nano-fibers [23]. Even in this case, however, the response was only 4% at a 50 ppm DMMP. Chang et al. worked on DMMP-sensing based on composites of multi-walled nanotubes (MWCNTs) and polyaniline, but their sensor was reported to show a response of 1% at 332 ppm DMMP [24]. These previous works indicate polyaniline could somehow play to reduce the response time whereas any single material of SWCNTs, MWCNTs, and polyaniline has a limited response. In this study, a DMMP gas detection method using a semiconducting SWCNT

---

* Corresponding authors.
E-mail addresses: wooyoung@yonsei.ac.kr (W. Lee), jinseonoh@gachon.ac.kr (J.S. Noh).

http://dx.doi.org/10.1016/j.snb.2014.11.137
0925-4005/© 2014 Published by Elsevier B.V.

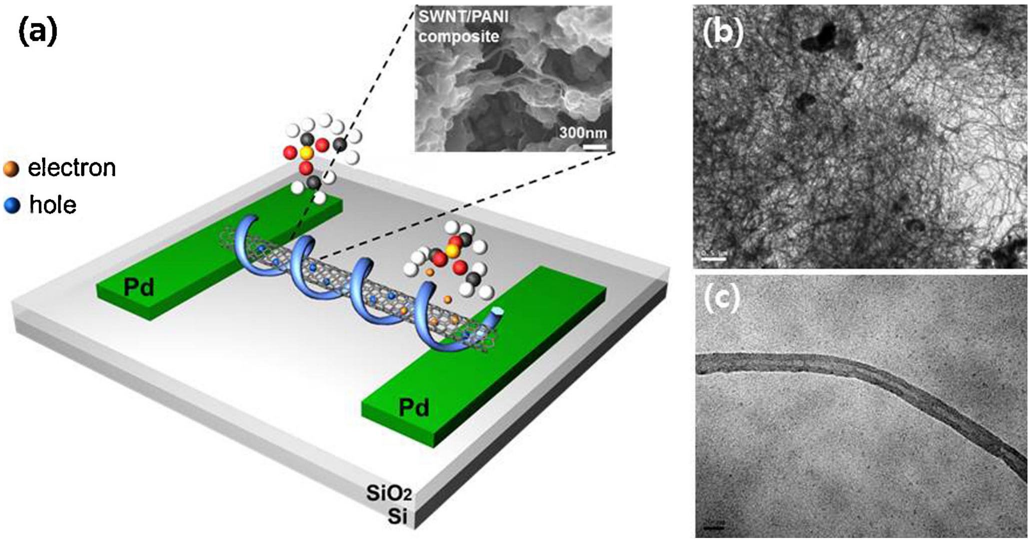

Fig. 1. (a) A schematic of an SWCNT–polyaniline composite sensor on an oxidized Si substrate with Pd electrodes. The inset shows an SEM image of the SWCNT–polyaniline composite. (b and c) TEM images of SWCNTs–polyaniline composite.

and conducting polyaniline composite was developed to solve the aforementioned problems. This composite sensor demonstrated very high response, rapid response time, high reproducibility, and room-temperature operability.

2. Materials and methods

2.1. Fabrication of SWCNT–polyaniline composite sensor

To fabricate the SWCNT–polyaniline composite sensors, a mixture solution of the SWCNT and the HCl doped polyaniline was dispersed on the patterned Pd electrode. First, the electrodes were patterned on a thermally oxidized Si substrates using photolithography and lift-off to prevent physical damage of CNTs. Here, the distance between two electrodes was ca. 32 μm. And 100 nm of Pd films were deposited on the patterned substrate. Pure arc discharge SWCNTs (70–90% purity; Hanwha Nanotech Co., Seoul, Korea) were dissolved in distilled (DI) water containing 0.2 wt% sodium dodecyl sulfate (SDS; Samchun Chemical Co., Gyeonggi-do, Korea) as a surfactant. After ultrasonification for 4 h, the SWCNTs were vacuum-filtered using Teflon filters (Millipore, pore size 20 μm) and rinsed with DI water for a few minutes to remove completely the SDS surfactant. Polyaniline was synthesized by the chemical oxidative polymerization of aniline monomers in an aqueous solution containing 1.33 M HCl and 2 M aniline [25]. Then HCl-doped polyaniline was dissolved in N,N′-dimethyl formamide (DMF; Sigma–Aldrich Chemical Co., St. Louis, USA) under an inert atmosphere. The prepared SWCNTs were added in this DMF solution containing HCl doped polyaniline, which solution was agitated for 24 h at room temperature for its uniform dispersion. The synthesized SWCNTs-polyaniline composite solution was dropped onto the patterned Pd electrode by using a micropipette.

2.2. Measurement

The setup constructed to analyze the response behavior of the SWCNT–polyaniline composite sensors to DMMP gas included a 180 cm^3 sealed chamber, mass flow controllers (MFCs) for air and target gases, and digital multimeters connected through a general-purpose interface bus (GPIB) to a computer. The DMMP gas concentration was adjusted by controlling its pressure relative to that of the ambient air. The real-time sensor resistance change was measured for 100 s in the presence of the target gas at a desired concentration before the chamber was evacuated for 100 s in preparation for another gas injection cycle. The SWCNT–polyaniline composite sensor was put onto a printed circuit board (PCB), electrically connected to it using silver paste, and was then loaded into a measurement chamber to evaluate its DMMP-sensing characteristics. All the measurements were performed at $\sim 25\,^{\circ}C$ with $28 \pm 5\%$ relative humidity, using N_2 as a carrier and vent gas. Real-time voltage was measured in the gas flow of varying DMMP concentrations, using a current source-measure unit (Keithley 236). Then the voltage was converted to resistance. Here, the resistance was defined as a voltage drop between two electrodes divided by an input current.

3. Results

Fig. 1(a) provides a schematic of the SWCNT–polyaniline composite dispersed on the oxidized Si substrate between Pd electrodes. Although a large number of SWCNT networks and polyaniline strands are present between the two electrodes, for simplicity, only a single polyaniline strand winding around one SWCNT is shown. A scanning electron microscope (SEM) image of the SWCNT–polyaniline composite is shown in the inset in Fig. 1(a). Fig. 1(b) exhibits the appearance of the overall composite and Fig. 1(c) shows a magnified strand of the SWCNT–polyaniline composite. These figures demonstrate that the polyaniline strand wrapped around the SWCNT exhibits good uniformity. Polyaniline forms an amorphous region with an uneven surface, a desirable feature for gas adsorption. Sensor response was recorded in real time by measuring the change in resistance of the composite film upon exposure to DMMP gas at room temperature. When an SWCNT–polyaniline composite sensor is exposed to the electron-donating gas DMMP, DMMP molecules are adsorbed onto and interact with the composite, stimulating electron transfer to the composite, as shown in Fig. 1. This increases the resistance of the composite because the majority carrier (hole) density in both SWCNTs and HCl-doped polyaniline is decreased by the transferred electrons.

Fig. 2(a) shows the real-time cyclic response of an SWCNT–polyaniline composite sensor to 10 ppm DMMP gas. The response of the SWCNT–polyaniline sensor is defined as

$$\text{Response}\,(\%) = \frac{R - R_0}{R_0} \times 100 \qquad (1)$$

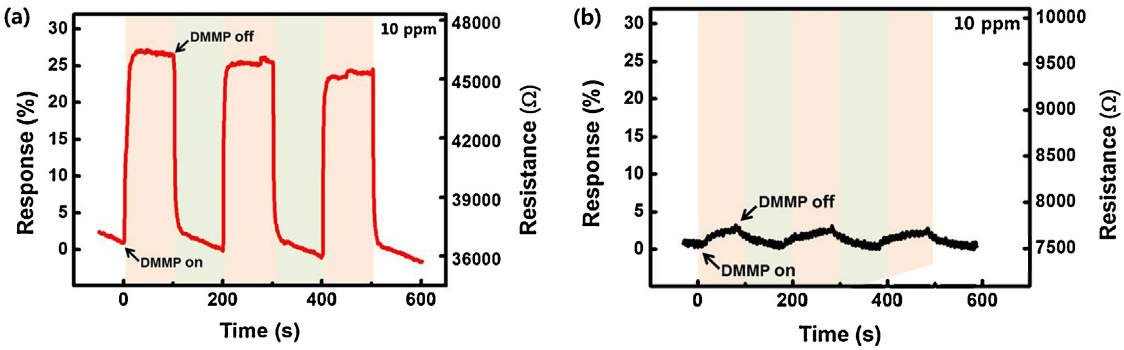

Fig. 2. Cyclic responses of (a) an SWCNT–polyaniline composite sensor and (b) a pure polyaniline to 10 ppm DMMP gas at room temperature. Gas flow injection and termination points are indicated by arrows.

where R_0 and R are the resistance before and after exposure to DMMP, respectively. The DMMP gas flow injection and termination points are marked in Fig. 2 data. As explained above, the resistance of the composite increases rapidly as DMMP gas enters the chamber, and decreases when the gas flow is blocked, enabling reversible response cycling. Comparing the composite sensor response behavior with that of pure SWCNT network sensors previously reported [18], SWCNT–polyaniline composite sensors exhibit a significantly greater apparent resistance change. For DMMP gas concentrations of 10 ppm, the composite sensor response (27.1%) is more than an order of magnitude larger than that of previous pure SWCNT network sensors (2.1%). Furthermore, the composite sensor response time (5.5 s) is about one-third of that of pure SWCNT network sensors (15 s). Response time is defined as the time to reach 90% of the total resistance change. We performed a similar cyclic response test on pure polyaniline and the result is shown in Fig. 2(b). The switching signal is not as clear as for the composite sensor, and the response (2.7%) is smaller than that of the composite sensor by about an order of magnitude. Moreover, the response time of polyaniline (65 s) is much longer compared to the composite sensor. These results indicate the significant improvement in DMMP-sensing properties of the composite sensor does not originate dominantly from any single material component, but is enabled by cooperative plays of the two materials. The significantly improved DMMP-sensing performance most likely arises from the effective carrier collection and rapid carrier transport empowered by the effective combination of SWCNTs and polyaniline, which play better as carrier-transporting channels and a carrier collector, respectively. In the SWCNT–polyaniline composite structure, the large empty space between adjacent SWCNTs is filled with polyaniline, increasing current conduction and decreasing the energy barrier for charge transport across neighboring SWCNTs. The detailed composite sensor sensing mechanism will be discussed later in comparison with pure SWCNT network sensors.

The SWCNT–polyaniline composite sensor response was examined at various DMMP concentrations at room temperature. Fig. 3(a) shows the real-time sensor sensitivities at various DMMP concentrations. The response clearly increases linearly with increased DMMP concentration, as summarized in Fig. 3(b). The response is well-scaled for a low DMMP concentration range, although the scaling trend is not monotonic. The linear correlation between SWCNT–polyaniline sensor response and DMMP concentration arises from the frequency of DMMP adsorption is generally proportional to its concentration. Reliable and rapid detection of trace amounts of DMMP is paramount when the deadliness of the gas is considered. In this respect, the large apparent response curve (response: 10.5%) for 1 ppm DMMP and the response versus DMMP concentration slope demonstrates the superior functionality of our SWCNT–polyaniline composite sensor in an infinitesimal DMMP concentration range.

4. Discussions

Fig. 4 shows a schematic comparison between the DMMP-sensing mechanisms in SWCNT–polyaniline composites and pure SWCNT network sensors. In a pure SWCNT network sensor, DMMP molecules donate electrons to SWCNTs during interactions between DMMP and the SWCNT strand. This interaction generally increases when the ends of SWCNTs are functionalized, typically with a carboxyl group (–COOH). The donated electrons locally transport through SWCNT strands, decreasing the SWCNT local hole

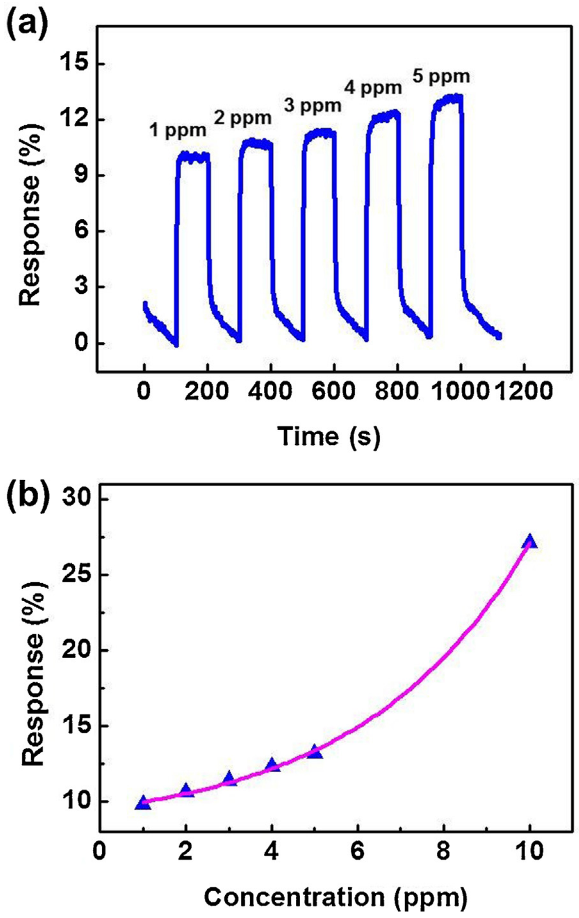

Fig. 3. (a) Real-time response curves as a function of DMMP concentration at room temperature and (b) response versus DMMP concentration.

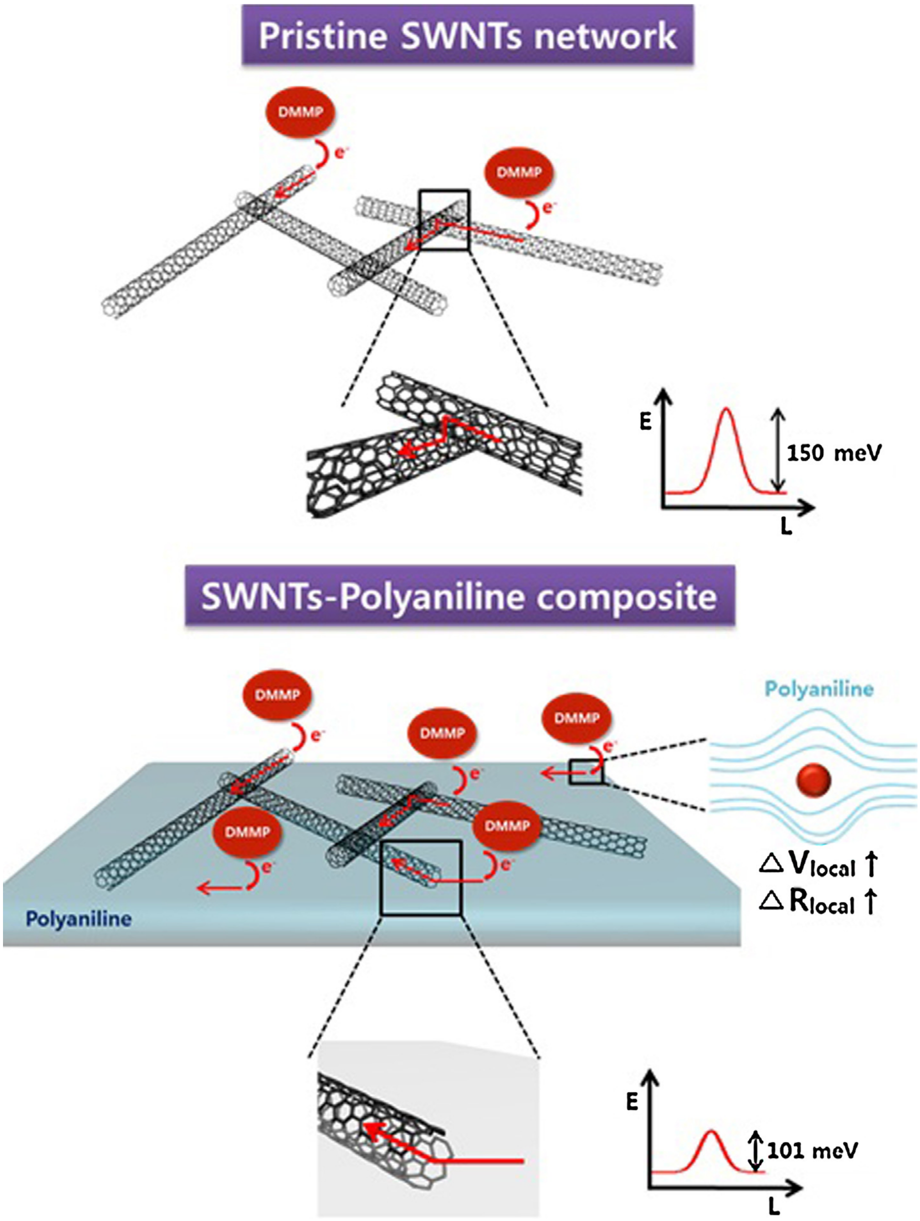

Fig. 4. Illustration of DMMP-sensing mechanism in pure SWCNT network sensors (top) and SWCNT–polyaniline composite sensors (bottom). The top panel inset shows a magnified view of two crossed SWCNTs and the corresponding energy barrier. The bottom panel lower inset magnifies the SWCNT–polyaniline interface and corresponding energy barrier; the right inset shows the distortion of the polyaniline matrix around an adsorbed DMMP molecule.

density and thus increasing the resistance. The limited number of SWCNT-DMMP interactions and relatively large energy barrier (~150 meV) [26] for crossing SWCNT strands restrict the response and response time of SWCNT network sensors.

In contrast, DMMP molecules are easily adsorbed onto polyaniline, which occupies the vast empty spaces between SWCNTs in SWCNTs-polyaniline composite sensors. The adsorbed DMMP molecules have two functions. First, they provide the polyaniline chains with electrons, thus reducing the density of positively charged polarons and thereby increasing the polyaniline resistance. Second, they increase the local polyaniline resistance by widening the gap between polyaniline chains near the adsorption site. In SWCNT–polyaniline composite sensors, electrons transfer from polyaniline to SWCNTs more than they transport directly from DMMP to SWCNTs. Electrons entering the SWCNT increase the SWCNT resistance by the mechanism explained above. The polyaniline-to-SWCNT electron transfer energy barrier is lower (~101 meV) than that of the crossing SWCNT strands mentioned above [27]. Therefore, the response and response time afforded by SWCNT–polyaniline composite sensors area large improvement over pure SWCNT network sensors. As shown in Fig. 2(b), polyaniline itself can detect DMMP molecules. However, its response to DMMP is about an order of magnitude smaller than that of SWCNT–polyaniline composite sensor and its response time is much longer. This indicates polyaniline alone cannot account for the sensing performance observed in the composite sensor. Although polyaniline plays as a main electron collector due to its dominant volume fraction occupied in the composite sensor, its conductivity is far lower compared to SWCNTs. Moreover, polyaniline tends to strongly interact with SWCNTs through π–π interactions [28]. These lead to electron transfer from polyaniline to SWCNTs, where the transferred electrons locally modify the majority carrier distribution. Since the energy barrier from polyaniline to SWCNTs is smaller than that for the SWCNT-to-SWCNT transfer as discussed, both the response and the response time of the composite are significantly improved compared to single material sensors like a SWCNTs sensor and a polyaniline sensor. In addition, besides the aforementioned electron transfer mechanism, the adsorption processes also can affect the response time of the sensor. Specifically, chemical and physical absorptions of DMMP on PANI [29] and MWCNT–PANI [24], respectively, are possibly related to the response time. Two absorption processes on SWCNT–PANI, although intimately related to the performance of the sensor, encourage further study.

5. Conclusion

The response behavior of SWCNT–polyaniline composite sensors to DMMP gas in air at room temperature was investigated. These sensors showed a much higher sensitivity and shorter response time than those of pure SWCNT network sensors and polyaniline sensors at a given DMMP concentration because the combination of SWCNTs and polyaniline enabled superior carrier collection and fast carrier transport. Electrons donated by DMMP molecules are collected mainly by polyaniline, which occupies most of the total volume, and the rapid electron collection and local transport causes a fast resistance increase. Furthermore, the SWCNT–polyaniline composite sensors showed good reproducibility and a linear correlation between sensitivity and DMMP concentration, enabling DMMP detection at lower than 1 ppm. These results suggest that SWCNT–polyaniline composites can be an ideal sensing material for DMMP gas.

Acknowledgments

This work was supported by the Agency for Defense Development (ADD) of the Republic of Korea, the Priority Research Centers Program (2009-0093823).

References

[1] F. Worek, M. Koller, H. Thiermann, L. Szinicz, Toxicology 214 (2005) 182–189.

[2] N.J. Choi, Y.S. Lee, J.H.A. Kwak, J.S. Park, K.B. Park, K.S. Shin, H.D. Park, J.C. Kim, J.S. Huh, D.D. Lee, Sens. Actuators B 108 (2005) 177–183.

[3] S.M. Kanan, A. Waghe, B.L. Jensen, C.P. Tripp, Talanta 72 (2007) 401–407.

[4] D.C. Meier, C.J. Taylor, R.E. Cavicchi, E. White, V.M.W. Ellzy, K.B. Sumpter, S. Semancik, IEEE Sens. J. 5 (2005) 712–724.

[5] R.C. Thomas, H.C. Yang, C.R. DiRubio, A.J. Ricco, R.M. Crooks, Langmuir 12 (1996) 2239–2246.

[6] R.A. McGill, V.K. Nguyen, R. Chung, R.E. Shaffer, D. DiLella, J.L. Stepnowski, T.E. Mlsna, D.L. Venezky, D. Dominguez, Sens. Actuators B 65 (2000) 10–13.

[7] D.D. Dominguez, R. Chung, V. Nguyen, R.A. Tevault, Sens. Actuators B 53 (1998) 186–190.

[8] G.M. Milner, Proc. SPIE 5778 (2005) 305–316.

[9] C. Zimmermann, P. Mazein, D. Rebiere, C. D'ejous, J. Pistr'e, R. Planade, IEEE Sens. J. 4 (2004) 479–488.

[10] Y. Yang, H. Ji, T. Fand Thundat, J. Am. Chem. Soc. 125 (2003) 1124–1125.

[11] C. Karnati, H.W. Du, H.F. Ji, X.H. Xu, Y. Lvov, A. Mulchandani, P. Mulchandani, W. Chen, Biosens. Bioelectron. 22 (2007) 2636–2642.

[12] M. Meyyappan, Carbon Nanotubes: Science and Applications, CRC Press, Boca Raton, FL, 2005.

[13] J. Li, Y. Lu, Q. Ye, L. Delzeit, M. Meyyappan, Electrochem. Solid-State Lett. 8 (2005) H100.

[14] Chen Wei, Liming Dai, Ajit Roy, Tia Benson Tolle, J. Am. Chem. Soc. 128 (2006) 1412–1413.

[15] A. Peigney, Ch. Laurent, E. Flahaut, R.R. Bacsa, A. Rousset Pcarbon, Carbon 39 (2001) 507–514.

[16] Cristian Staii, Alan T Johnson Jr., Nano Lett. 5 (9) (2005) 1774–1778.

[17] K.H. An, S.Y. Jeong, H.R. Hwang, Y.H. Lee, Adv. Mater. 16 (12) (2004).

[18] Y.J. Kim, S.H. Lee, H.H. Choi, J.S. Noh, W.Y. Lee, Nanotechnology 21 (2010) 495501.

[19] Y. Wang, Z. Zhou, Z. Yang, X. Chen, D. Xu, Y. Zhang, Nanotechnology 20 (2009), 345502 (8 pp.).

[20] P. Bondavalli, P. Legagneux, D. Pribat, Sens. Actuators B 140 (1) (2009) 304–318.

[21] J.P. Novak, E.S. Snow, E.J. Houser, D. Park, J.L. Stepnowski, R.A. McGill, Appl. Phys. Lett. 83 (19) (2003) 4026–4029.

[22] E.S. Snow, F.K. Perkins, E.J. Houser, S.C. Badescu, T.L. Reinecke, Science 307 (2005) 1942.

[23] S. Cho, O. Kwon, S. You, J. Jang, J. Mater. Chem. A 1 (2013) 5679.

[24] C.-P. Chang, C.-L. Yuan, J. Mater. Sci. 44 (2009) 5485–5493.

[25] H.H. Choi, J.M. Lee, K.Y. Dong, B.K. Ju, W.Y. Lee, Macromol. Res. 20 (2) (2012).

[26] D.H. Kim, J. Huang, H.K. Shin, S. Roy, W. Choi, Nanoletters 6 (12) (2006) 2821–2825.

[27] S.B. Kondawar, M.D. Deshpande, S.P. Agrawal, Int. J. Composite Mater. 2 (3) (2012) 32–36.

[28] Q. Yao, L. Chen, W. Zhang, S. Liufu, X. Chen, ACS Nano 4 (4) (2010) 2445–2450.

[29] S. Cho, O.S. Kwon, S.A. You, J. Jang, J. Mater. Chem. A 1 (2013) 5679.

Biographies

Ran Yoo earned her Master's degree in 2013. She is currently studying on the nerve agent gas sensor using carbon nanotubes or metal oxide towards her ME in Nerve Agent Gas sensor at Yonsei University.

Jeongmin Kim earned he Bachelor's degree in 2008. He is currently studying on the thermoelectricity using Bi based nanowire towards his ME in thermoelectricity at Yonsei University.

Min-Jung Song received her PhD in chemical engineering from Korea University (2007). Now, she is working as a Research Professor at Yonsei University. Her research interests are focused on the bio-sensors, electroanalysis, and bio-MEMS.

Jin-Seo Noh is a Professor of Department of Nano-Physics at Gachon University. He earned his bachelor's degree in 1991 and Master's degree in 1993 from Korea University, Korea. He earned his Ph.D. degree in materials science in 2003 from the University of Wisconsin-Madison. He has been with the Samsung Advanced Institute of Technology (SAIT) as a member of research staff in 2003–2008, where he performed research on next-generation memories and logic devices. He spent another year working on 28 nm technology development at the System LSI Division of Samsung Electronics. In 2009, he was appointed as a Research Professor to the Institute of Nanoscience and Nanotechnology of Yonsei University. His current research interests include nanomaterials-based thermoelectric energy conversion, nano electronics/spintronics, nanostructures-utilizing hydrogen gas and toxic gas sensors, and technology fusion crossing the borders. He has been appointed a faculty member of the Department of Nano-Physics at Gachon University.

Wooyoung Lee is a Professor of Department of Materials Science and Engineering, the Chairman of Yonsei Institute of Convergence Technology and the Head of Institute of Nanoscience and Nanotechnology at Yonsei University in Korea. He received a BS degree in metallurgical engineering in 1986, a MS degree in metallurgical engineering from the Yonsei University in 1988. He received a Ph.D. degree in physics from University of Cambridge, England in 2000. He is also the director in Korea-Israel Industrial R&D Foundation and the Advisor in National Assembly Research Service. In recent years, his research interests have centered on thermoelectric devices, spintronics, hydrogen sensors and hydrogen storage materials. He has received a number of awards in nano-related research areas and a Service Merit Medal (2008) from the Korean Governments due to contribution on the development of intellectual properties. He has authored and co-authored over 150 publications, and has edited a few of special books on nano-structured materials and devices.