Talanta 85 (2011) 463–468

Contents lists available at ScienceDirect

Talanta

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

Sensing properties of polyethylenimine coated carbon nanotubes in oxidized oil

Vincent Lau Chun Fai, Yang Doo Lee, Kyongsoo Lee, Keun-Soo Lee, Dae-Jin Ham, Byeong-Kwon Ju*

Display and Nanosystem Laboratory, College of Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea

ARTICLE INFO

Article history:
Received 20 December 2010
Received in revised form 3 April 2011
Accepted 4 April 2011
Available online 9 April 2011

Keywords:
Carbon nanotube
Polyethylenimine
Oxidized oil
Chemical sensor

ABSTRACT

Chemical detection is still a continuous challenge when it comes to designing single-walled carbon nanotube (SWCNT) sensors with high selectivity, especially in complex chemical environments. A perfect example of such an environment would be in thermally oxidized soybean oil. At elevated temperatures, oil oxidizes through a series of chemical reactions that results in the formation of monoacylglycerols, diacylglycerols, oxidized triacylglycerols, dimers, trimers, polymers, free fatty acids, ketones, aldehydes, alcohols, esters, and other minor products. In order to detect the rancidity of oxidized soybean oil, carbon nanotube chemiresistor sensors have been coated with polyethylenimine (PEI) to enhance the sensitivity and selectivity. PEI functionalized SWCNTs are known to have a high selectivity towards strong electron withdrawing molecules. The sensors were very responsive to different oil oxidation levels and furthermore, displayed a rapid recovery of more than 90% in ambient air without the need of heating or UV exposure.

1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have shown a great amount of potential for molecular detection. Recently, researchers have even shown that CNTs are able to detect chemical concentrations of up to several ppb [1]. These highly sensitive sensors can be applied to various fields, ranging from chemical, medical, environmental, industrial, and homeland security [1–3]. However, in order to be of practical use, researchers must first improve the selectivity of the CNTs. Most CNT experiments are carried out in controlled environments where the sensors are only exposed to the target analyte without the presence of other interference chemicals. In thermally oxidized soybean oil, sensors are constantly exposed to dozens of chemicals at the same time and the presence of interference with our target analyte is practically unavoidable. Multiple contributors can influence the response of the sensor, thus making selectivity to a specific group of chemicals extremely important.

Our work focuses on developing a room-temperature sensor for detecting the oxidation levels of soybean oil. Oxidation can occur in ambient conditions but at elevated temperatures, this process is accelerated. Frying is one of the most common methods for food preparation, because of its resultant desirable texture and savory flavor. However, repeated use of the oil produces chemical constituents that can be detrimental to health [4]. The science of frying is a very complex process due to the continuous or repeated heating to high temperatures of around 180–200 °C. The chemical reactions that take place at these temperatures are hydrolysis, oxidation, polymerization, and pyrolysis. Therefore, numerous studies have been dedicated to identifying the products of these reactions in order to fully understand the health effects of oxidized oil in the human body. Among the major groups, which have been identified are monoacylglycerols, diacylglycerols, oxidized triacylglycerols, dimers, trimers, polymers, hydroperoxides, free fatty acids, ketones, aldehydes, alcohols, and esters [5,6]. As the oil oxidizes at high temperatures, volatile components such as ketones, aldehydes, and alcohols will volatize leaving behind accumulated large polymers, polar compounds, and free fatty acids. Continuous accumulation of these products can cause adverse health effects; therefore the oil needs to be discarded after a certain point in time. In order to determine the oxidation level at which to discard the used oil, numerous efforts have been carried out to quantify these oxidation products.

Currently, there are many analytical methods available to determine the oxidation level of oil, for example, the peroxide value, the iodine value, the free fatty acid value, the p-anisidine value, the TOTOX value, and the total polar material (TPM) value. In spite of that, most of these methods are time consuming and require expensive equipment for accurate results; therefore, these indexes are more often used in research studies rather than in regular quality control. In this paper, we will demonstrate a simple and quick method for detecting the oxidation level of soybean frying oil using polymer coated CNT sensors. The responses of these sensors are large and they recover more than 90% rapidly, making them suitable detection devices that can be deployed for quality control in the food industry. In this report, the free fatty acid value will be used as a gauge for the oxidation level of our oil samples because free fatty acids are one of the major acceptor molecules in the oxi-

---

* Corresponding author. Tel.: +82 2 3290 3237; fax: +82 2 3290 3791.
E-mail address: bkju@korea.ac.kr (B.-K. Ju).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.04.006

dized oil, which are detected by the sensor. Although TPM is an official AOCS method and is widely recognized as the most accurate method for assessing the degradation status of frying oils [7], we will demonstrate that the free fatty acid value of our oil samples has linear correlation with the TPM value.

2. Experimental

2.1. Sensors

1 mg of purified HIPCO SWCNTs, purchased from Unidym, were dispersed in 30 ml of *N*,*N*-dimethylformamide (DMF) and bath sonicated for 2 h. 10 ml of this solution was diluted with 56.6 ml of DMF to produce a concentration of 0.005 mg/ml. This dispersion was then centrifuged at 15,000 rpm for 15 min; only the top 20% of the dispersion was carefully decanted in order to reduce the number of SWCNT bundles. Previous works [8,9] have shown that the binding energy at the adsorption sites of the bundles is significant, which would make the recovery of the sensor difficult. Next, prefabricated glass substrates with Au as electrodes were heated to 170 °C and the SWCNT thin films were sprayed uniformly onto the substrates at a fixed distance of 2 cm using a spray gun (0.3 mm nozzle size) purchased from Air Factory. The density of the films were varied by spraying 0.3, 0.35 and 1 ml of 0.005 mg/ml SWCNT solution for the low (3.75 mg/m^2), medium (4.375 mg/m^2) and high (12.5 mg/m^2) density films respectively. The densities of the films can be approximated by considering the area exposed to the jet stream. In order to enhance the sensitivity and to impart selectivity to the sensors, we adsorbed polyethylenimine (PEI), purchased from Sigma Aldrich, onto the SWCNT network. A solution of 20 wt% PEI/methanol was prepared and the sensors were immersed for 2 h in the solution. The sensors were then rinsed with methanol to remove the excess PEI. The sensors were then heated at a temperature of 70 °C for 10 min in order to evaporate the methanol from the surface, leaving behind only the PEI coated SWCNT thin film. Similar sensors with different immersion time of 10 min, 1 h and 12 h were also fabricated to study the effects of PEI coating on the sensors.

2.2. Oil Samples

A common household soybean oil was purchased and heated in a silicon bath at temperatures of 180 ± 5 °C while being stirred with a magnetic bar in order to achieve uniformity. Several samples were extracted at different time intervals and were cooled down to room temperature. The acid value of each sample was measured by titration. The acid value indicates the oxidation level of the oil samples. A total of 5 samples, with the respective acid values of 0.2 (new oil), 0.8, 1.2, 1.6 and 2.0 mg KOH/g, were used for our experiment. European countries such as Spain, Portugal, France, Germany, Belgium, Switzerland, Italy, and the Netherlands have established regulatory limits for TPM in frying oil and most of these countries have set the limit to 25% [10]. Fig. 1 shows the linear relation between TPM free fatty acid values of our oil samples. Samples with an acid value of 2.0 mg KOH/g have a corresponding TPM value of 35.5%, which is well above the regulatory limit and are no longer suitable for consumption. Therefore, measuring the oxidation level of oil samples up to 2.0 mg KOH/g is sufficient for quality control applications in the food industry.

2.3. Measurements

2.3.1. Response of as-purchased and PEI coated SWCNTs in oxidized oil

As-purchased and PEI coated SWCNT sensors were immersed into each sample at room temperature for 5 min in an ascending order based on their acid values. After each immersion, the sensor were left to recover in ambient conditions for another 5 min. A second cycle was repeated for the PEI SWCNT sensor but this time, the immersion duration was extended to 10 min while maintaining the recovery time as before. Repeatability measurement was also conducted for the PEI coated sensor on a sample with an acid value of 1.6 mg KOH/g. The change in resistance was measured using a Keithley 2400 Sourcemeter at a DC bias voltage of 1 V.

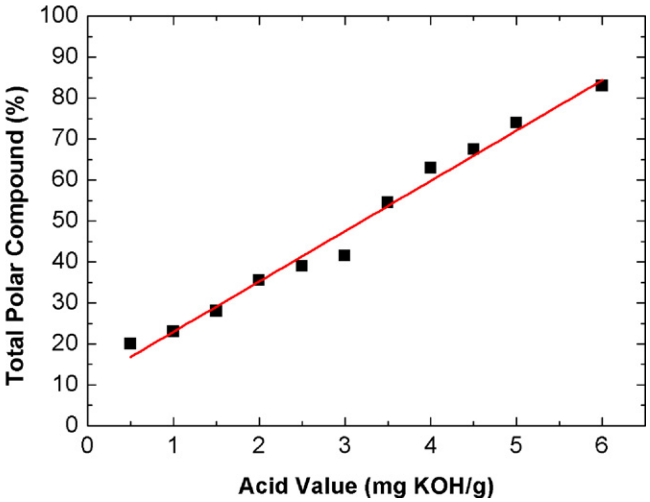

Fig. 1. Corresponding TPM values for the acid values of the oxidized oil samples.

2.3.2. Response of sensors in hexanal and acetic acid

In order to study the interaction of the PEI SWCNT sensor with oxidized oil, an experiment was devised involving two major chemical groups, aldehyde and carboxylic acid which are common oxidation products [5]. The responses of pristine and PEI SWCNT in hexanal and acetic acid were measured and compared.

2.3.3. PEI coating and SWCNT film density

All experiments mentioned till this point were carried out for medium density SWCNT films which have been immersed in PEI for 2 h. Sensors with different PEI immersion time and different SWCNT film densities were also immersed in the oxidized oil samples and the responses were compared.

3. Results and discussion

Experiments were first carried out to study the effects of the oil oxidation level on as-purchased purified SWCNTs. Fig. 2 shows the response of the sensor and its partial recovery curve. The descending trend observed here is most likely to be attributed to the increase in the amount of acceptor molecules, such as free fatty acids, produced as the oil oxidizes. Acids are known to act as electron acceptors, causing the resistance of the p-type SWCNT channel to decrease [11]. Free fatty acids have a similar effect on the SWCNT sensors. Despite the appearance of a trend, the undoped SWCNT sensor does not recover to its initial state after the first immersion. Heating the sensors and also rinsing the sensors with chemical solvents such as hexane and acetone did not remove the layer of oil coating the sensor and the initial value remained unrecoverable.

In order to improve the recovery of these sensors, the surface of the thin film SWCNT has to be chemically treated. SWCNTs when functionalized with PEI, as reported by Pengfei Qi et al., are highly selective to strong electron withdrawing molecules (acceptors) [2]. The direct adsorption of PEI onto SWCNT thin films causes the polymer to wrap around the SWCNTs. Complete desorption of this polymer from the SWCNT was not observed even through thor-

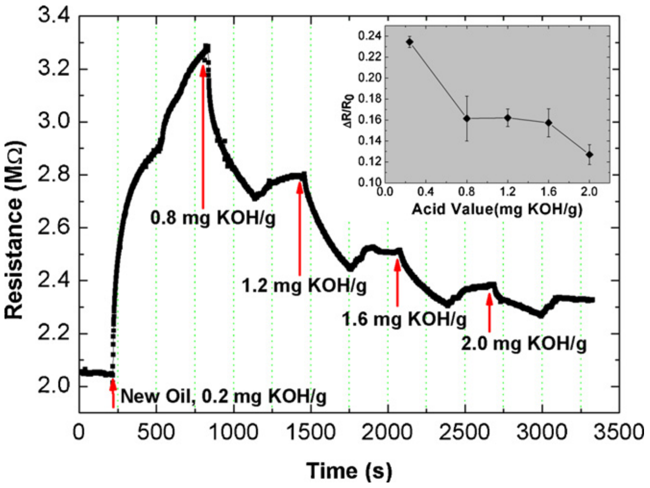

Fig. 2. Continuous response of the untreated SWCNT sensor immersed in oxidized oil samples with acid values from 0.2 to 2.0 mg KOH/g. The inset shows the average response of the untreated SWCNT sensors for each acid value. For each measurement, a different sensor was used to observe the consistency in the trend.

ough rinsing with ethanol. After the adsorption, the amine group from the PEI, which is known to react with carbon dioxide in the atmosphere to form carbamate, did not influence the electrical properties of the sensor. A previous report explained that the amine groups after adsorption become unavailable for the reaction because of their intimate interaction with the SWCNT [12]. XPS was used to analyze the interaction between PEI and the SWCNT network. Fig. 3(a) shows the C1s spectrum of the untreated SWCNT network whereas Fig. 3(b) and (c) shows the C1s and N1s spectra for the PEI-SWCNT after 2 h of immersion, respectively. The C1s spectrum of the PEI functionalized SWCNT shows a formation of a second peak at 285.1 eV in addition to the main C–C peak being shifted to a lower binding energy of 283.5 eV from the initial value of 284.0 eV for the untreated SWCNTs. This second peak with the higher binding energy is a result of the presence of the C–N bond in the PEI amine group [13]. A negative shift in the main C–C peak is rarely observed in the XPS spectrum of functionalized SWCNT [14]; nonetheless, the partial charge transfer between the SWCNT and the physisorbed donor PEI provides an explanation for this observation. Although there is a slight increase in the screening effect, the electrons in a partially negative SWCNT C atom would experience higher electron repulsion causing the binding energy to weaken compared to electrons in a neutral C, which results in a negative shift of the C–C peak. Further studies are needed to confirm this explanation for the negative shifts of the main peak. In the case of the N1s spectra (Fig. 3(c)), the peak did not indicate any formation of an amine linkage with the SWCNTs or the formation of carbamate with CO_2 in air. The N1s retained the sharp and symmetrical amines binding energy peak at 398.7 eV.

Fig. 4(a) and (b) shows the response of the PEI functionalized SWCNT sensor towards the oxidized oil samples after 5 and 10 min of immersion, respectively. Both measurements were carried out on the same sensor with a short time interval in between the two cycles in order to show the reproducibility of the decreasing trend. Fig. 4(c) compares the response magnitude of the sensor after 5 and 10 min of immersion. At an acid value of 1.8 mg KOH/g and beyond the response of the sensor started to saturate. The saturation in the response is due to the increase of the viscosity of the oxidized oil which slows down the charge transfer rate with the SWCNT network during the first few seconds of immersion. The sensor not only has a large response but also exhibited a rapid recovery of more than 90% in ambient conditions when extracted from the oil samples. Such a recovery is extremely desirable for low cost and energy efficient sensors because there is no need for external heating or UV exposure to induce desorption of the analytes. The reversibility of the sensor can be attributed to the PEI coating on the SWCNTs. The binding energy of the analytes is reduced by the adsorption on the surface of the PEI rather than directly on the SWCNT network [15]. The PEI basically acts as an intermediate charge transfer layer from the SWCNT to the electron acceptors, as depicted in Fig. 5. The repeatability of the measurement on a sample with a single acid value is shown in Fig. 4(d).

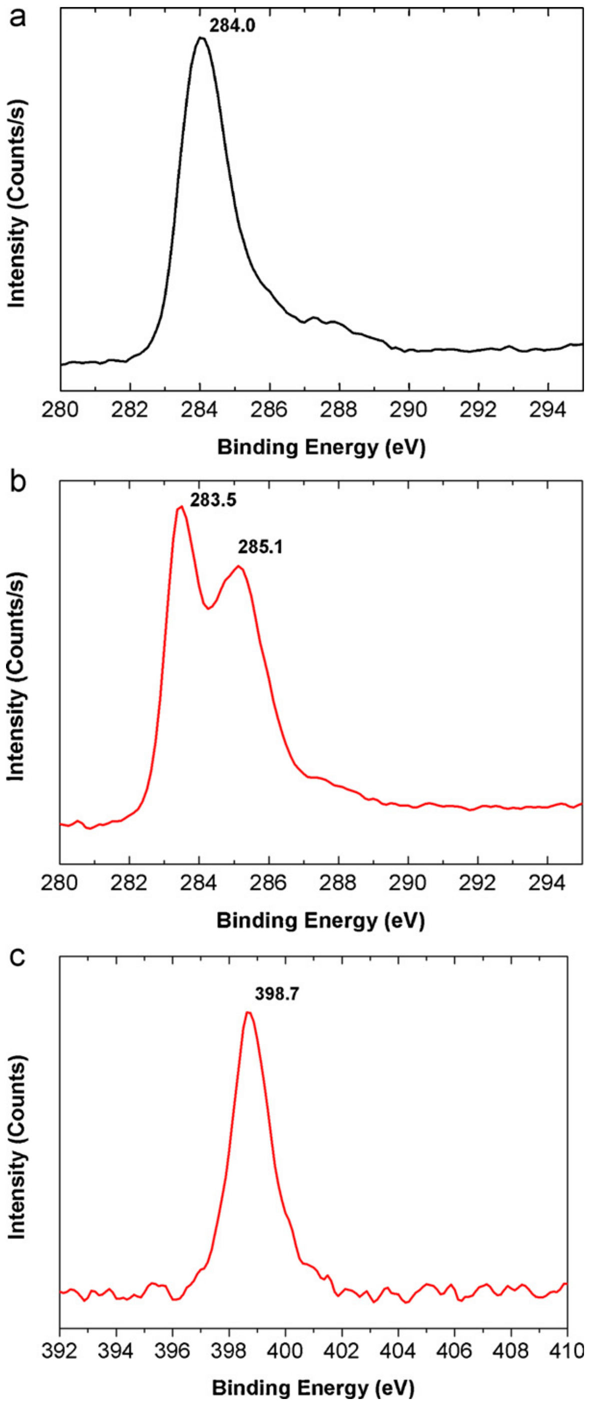

Fig. 3. XPS spectra of the SWCNT samples: (a) the C1s spectrum of untreated SWCNTs, (b) the C1s spectrum, and (c) the N1s spectrum of SWCNTs after 2 h of immersion in PEI.

Fig. 6 compares the responses of p-type pristine SWCNTs and PEI coated SWCNTs in hexanal and acetic acid. Pristine SWCNT

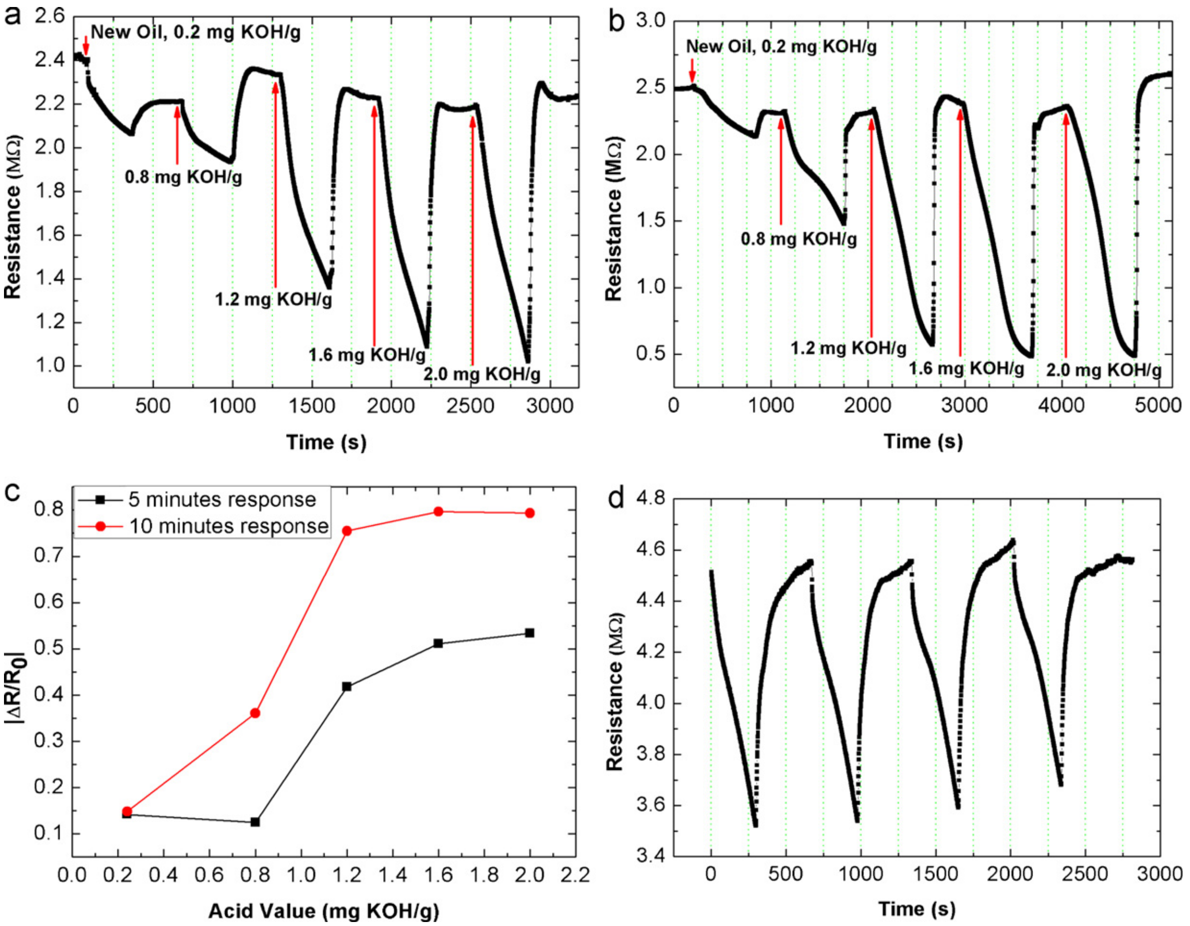

Fig. 4. Response of a single PEI functionalized SWCNT sensor immersed for (a) 5 and later (b) 10 min in the oxidized oil samples. The recovery of the sensor was carried out in room temperature air. (c) The comparison of the response magnitude, $|\Delta R/R_0|$ for the sensor immersed for 5 and 10 min. Saturation is observed after 1.8 mg KOH/g. (d) Repeatability of the sensor was demonstrated in sample with acid value 1.6 mg KOH/g.

exhibited an initial rise in conductance which can be attributed to partial charge transfer with the electron acceptor analytes. However, due to gradual swelling of the SWCNT film which follows, the conductance begins to drop below the initial point and saturates. These sensors were also unrecoverable in ambient conditions. In the case of PEI SWNT films, a similar initial rise in conductance was observed but due to the limited swelling effect of the film and also effective charge transfer, the conductance saturates above the initial point. Acetic acid shows a greater increase in conductance than hexanal because acetic acid is a stronger electron acceptor. The overall rise in conductance indicates that PEI provides better selectivity for electron acceptors and at the same time limit the effects of swelling. Recovery of these sensors was also possible.

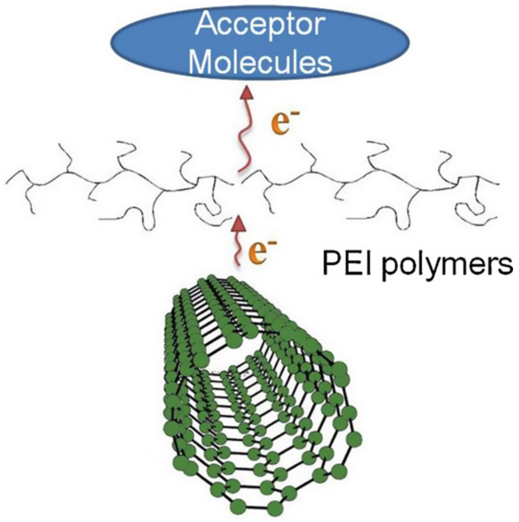

Fig. 5. PEI coating reduces the number of high binding energy sites by acting as an intermediate layer for a charge transfer between the electron acceptors and the SWCNT.

In previous reports [12,15,16], PEI coated SWCNTs were said to display n-type properties if sufficiently doped. Thus, in order to control the doping level of the SWCNT network, the sensors were immersed in a PEI/methanol solution for 10 min, 1 h, 2 h and 12 h. The sensors submerged for 10 min showed a similar response to the untreated SWCNT sensors and were not recoverable. The reason for such similarities might be due to the ineffective PEI coating of the SWCNT network at the early stages of the immersion. After 1 and 2 h of immersion, both sensors showed similar responses as shown previously in Fig. 4(a). As expected, there was a large increase in the initial resistance of these sensors, due to the donor effects of the PEI on the p-type SWCNT channel. Electron acceptors in the oxidized oil samples, such as free fatty acids, are selectively adsorbed onto the PEI functionalized SWCNT and charge transfer takes place from the SWCNT to the acceptors with PEI acting as an intermediate. The partial electron transfer from the SWCNT results in a decrease in the resistance; the magnitude of this resistance drop increases as the oxidation level of the oil increases. In order to convert the p-type channel of the SWCNT to an n-type, the sensors were immersed overnight for approximately 12 h. However,

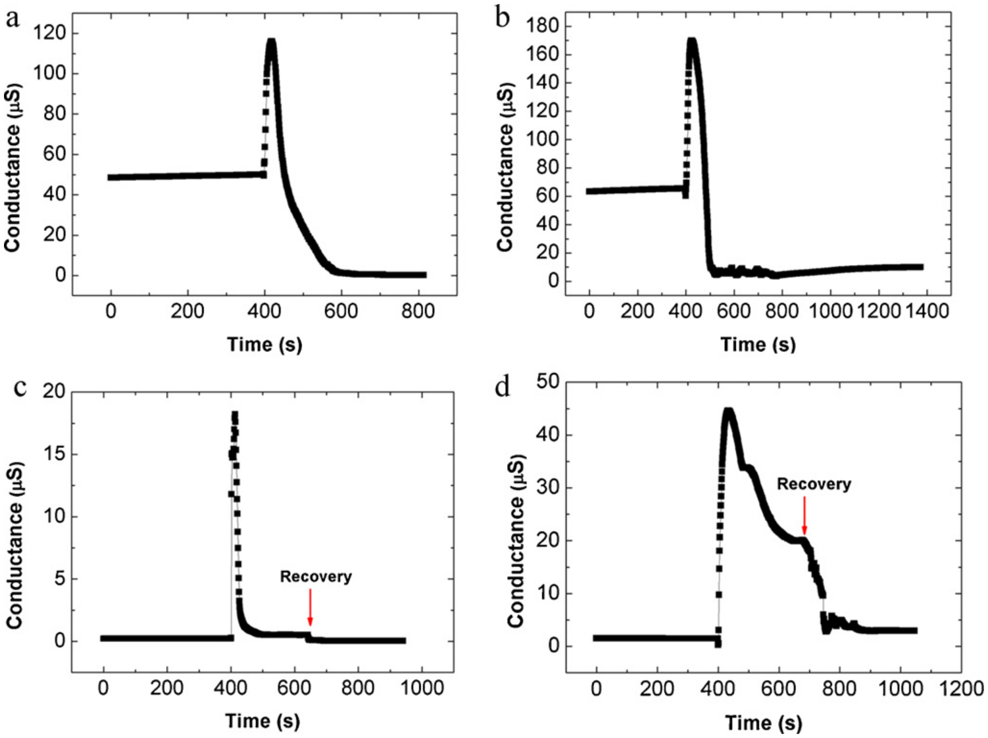

Fig. 6. Response of pristine SWCNT in (a) hexanal and (b) acetic acid. Response of PEI SWCNT in (c) hexanal and (d) acetic acid.

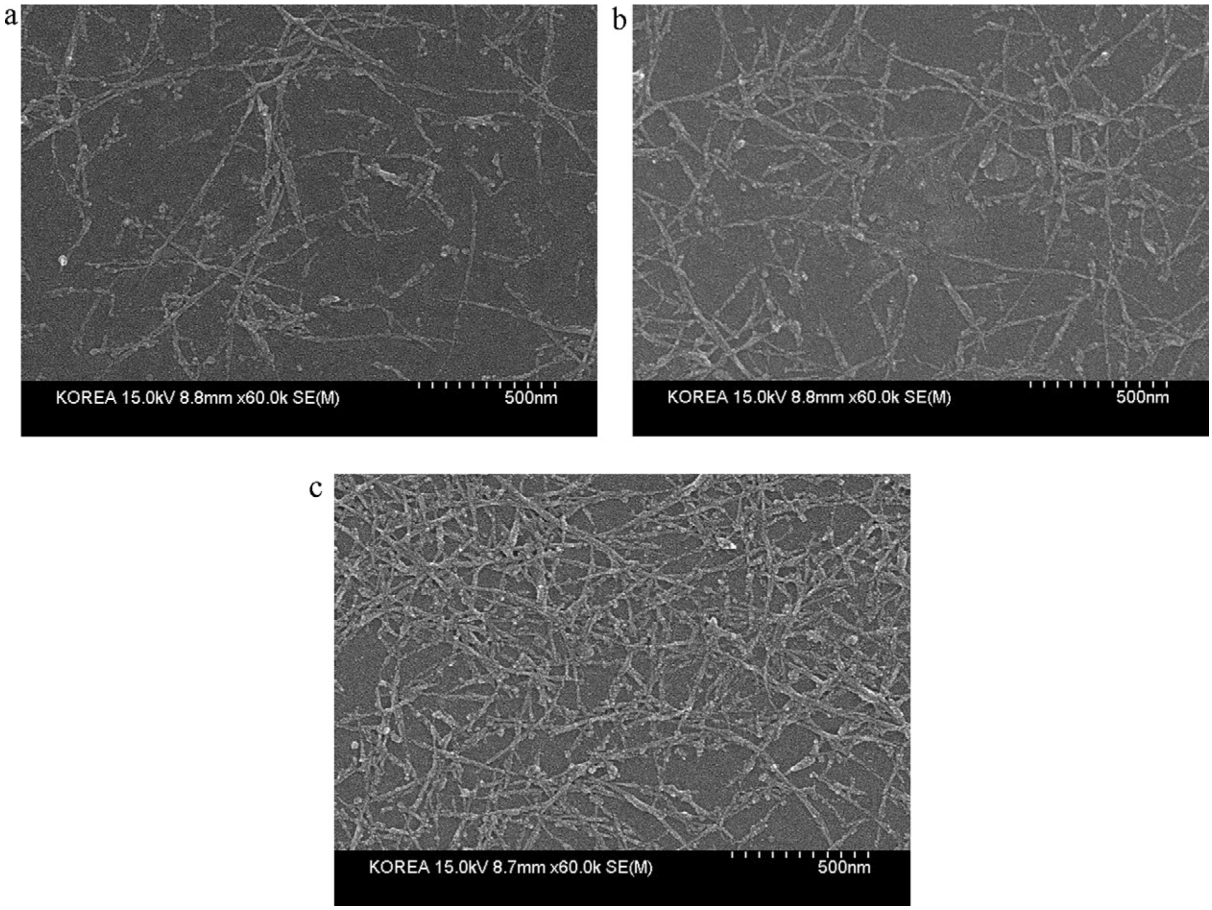

Fig. 7. Scanning electron microscope images of the (a) low (3.75 mg/m^2), (b) medium (4.375 mg/m^2), and (c) high (12.5 mg/m^2) density SWCNT network.

Table 1
Summary of the recoverability of the sensors with different SWCNT network densities.

SWCNT network density	Low	Medium	High
	(3.75 mg/m^2)	(4.375 mg/m^2)	(12.5 mg/m^2)
Initial resistance after immersion in PEI (Ω)	~100 M	~2 M	~10 K
Recovery	No	Yes	No

after the immersion, the sensors lost their recoverability and sensitivity. The exact mechanism which caused the loss of the sensor's characteristics is not clear; however we have deduced two possible reasons which could lead to such phenomena. The first reason could be due to the basicity of the amine group in PEI. Different levels of basicity could influence the selectivity of the analytes that interact with the PEI functionalized SWCNT [15]. The other reason may be due to the agglomeration of the PEI polymer over the SWCNT network after long hours of immersion. The formation of a thick coating of PEI polymer around the SWCNT could disable the sensitivity of the SWCNT towards the charge transfer between the outer layer PEI and acceptor molecules.

The densities of the PEI functionalized SWCNT thin films were also varied in order to investigate the effects of the network density on the recoverability of the sensors (Table 1). At a low SWCNT density (Fig. 7(a)), the response towards the oxidized oil was undetectable. The SWCNT network is near the percolation threshold and thus the overall resistance is dominated by the tube–tube or bundle–bundle contact resistance [17]. Even if the charge transfer happens and the resistance of the SWCNT changes, the effect on the overall resistance of the sensor is negligible. At the medium density (Fig. 7(b)), the sensors showed a relatively large response towards the oxidized oil. As the density increases, the SWCNT network moves above the percolation threshold and the number of low resistance intertube junctions starts to increase. At this point, the overall resistance will no longer be dominated by the high junction resistance but will also be affected by the resistance change on the SWCNT tubes themselves, thereby explaining the large response of these sensors. At the higher densities (Fig. 7(c)), the effective adsorption of the PEI on the SWCNTs only happens on the surface because of the highly bundled and multilayered SWCNT network. Similar to the low PEI doping concentration, the sensors behave like an untreated SWCNT network.

4. Conclusion

Despite the fact that the molecules detected by the PEI-SWCNT sensors were not specifically identified in our work, the decreasing resistance trend of the sensor as the acid value increased and the rapid recovery of more than 90% in ambient conditions suggest that PEI-SWCNT is able to selectively detect acceptor molecules regardless of the extremely complex chemical environment. Nonetheless, to achieve such selectivity and recovery, the doping concentration and the network density have to be taken into consideration. By controlling doping concentration and the basicity of the SWCNT network, the PEI-SWCNT sensors can be deployed in various fields and the sensitivity of the sensor can be configured based on the different chemical environments.

Acknowledgements

This research was supported by Seoul Metropolitan Government through Seoul Research and Business Development (grant no. PA090685).

References

[1] G. Peng, U. Tisch, H Haick, Nano Lett. 9 (2009) 1362–1368.
[2] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, K.J. Cho, Nano Lett. 3 (2003) 347–351.
[3] Y. Wang, Z. Zhou, Z. Yang, X. Chen, D. Xu, Y Zhang, Nanotechnology 20 (2009) 345502.
[4] C.M. Seppanen, A.S. Csallany, JAOCS 79 (2002) 1033–1038.
[5] G. Picariello, A. Paduano, R. Sacchi, F Addeo, J. Agric. Food Chem. 57 (2009) 5391–5400.
[6] S.M. Mahungu, S.L. Hansen, W.E. Artz, J. Agric. Food Chem. 47 (1999) 690–694.
[7] M.M. Blumenthal, Food Technol. 45 (1991) 68–71.
[8] M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsky, M. Muris, M.R. Johnson, T. Wilson, M. DePies, O.E. Vilches, Phys. Rev. B 70 (2004) 035410.
[9] A.J. Zambano, S. Talapatra, A.D. Migone, Phys. Rev. B 64 (2001) 075415.
[10] D Firestone, Inform 4 (1993) 1366–1371.
[11] C. Klinke, A. Afzali, P Avouris, Chem. Phys. Lett. 430 (2006) 75–79.
[12] J. Kong, H Dai, J. Phys. Chem. B 105 (2001) 2890–2893.
[13] T. Ramanathan, F.T. Fisher, R.S. Ruoff, L.C. Brinson, Chem. Mater. 17 (2005) 1290–1295.
[14] T.I.T. Okpalugo, P. Papakonstantinou, H. Murphy, J. McLaughlin, N.M.D Brown, Carbon 43 (2005) 153–161.
[15] C.Y. Lee, M.S. Strano, J. Am. Chem. Soc. 130 (2008) 1766–1773.
[16] M. Shim, A. Javey, N.W.S. Kam, H. Dai, J. Am. Chem. Soc. 123 (2001) 11512–11513.
[17] E. Bekyarova, M.E. Itkis, N. Cabrera, B. Zhao, A. Yu, J. Gao, R.C. Haddon, J. Am. Chem. Soc. 127 (2005) 5990–5995.