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SWNT Sensors for Monitoring the Oxidation of Edible Oils

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***Abstract*—**There are several means to measure the oxidation of edible oils, such as the acid value, the peroxide value, and the anisidine value. However, these means require large quantities of reagents and are time-consuming tasks. Therefore, a more convenient and time-saving way to measure the oxidation of edible oils is required. In this report, an edible oil condition sensor was fabricated by using single-walled nanotubes (SWNT). In order to test the sensor, oxidized edible oils, each one at a different acid value, were prepared. The SWNT sensors were immersed into these oxidized oils and the resistance changes in the sensors were measured. It was found that the conductivity of the sensors decreased as the oxidation level of oil increased. This result suggests that a change of the oil components induced by the oxidation process in edible oils is related to the conductivity change in the SWNT sensor.

***Keywords*—**Single-walled carbon nanotubes; edible oil oxidation; chemical sensor.

I. Introduction

CARBON nanotubes (CNTs) have been widely studied since they were first discovered by Iijima in 1991[1]. Due to their outstanding electrical properties, such as their high current densities, high electrical conductivity, and high sensitivity, they are sure to be spotlighted in future nanotechnology. Among their other attributes, single wall nanotubes (SWNTs) posses good sensitivity at room temperature, which holds great prospects in many future sensing applications[2-5].

Edible oils, such as soybean oil or corn oil, are one of the most widely used food sources and are essential to our food culture. However, when the oils are used repeatedly, many undesirable edible oil oxidation products, some of which may cause health problems, are generated[6]. The principle components of edible oils are triglycerides(TAGs)[7], an ester that consists of a glycerol backbone combined with three fatty acids. When the edible oils are used, the triglycerides decompose due to a hydrolysis mechanism[8] and oxidation organic compounds harmful to human health are produced. Consequently, it is very important to repeatedly monitor the used oils to ensure that they are still viable. There are many methods used to determine the degree of oxidation in edible oils, such as the acid value, the peroxide value, or the anisidine value[9] However, these methods are time-consuming and inconvenient; it is necessary to create a more convenient and time-saving method. In this work, a sensor using SWNTs to detect the degradation of edible oils was fabricated. As stated above, the oxidation of edible oils causes the generation of oxidation organic compounds, such as aldehydes, alcohols, hydrocarbons, and carboxylic acids. These oxidation materials are absorbed into the SWNT and change the conductivity of the SWNT channels via charge transfer mechanism [3] The SWNT oil condition sensor was fabricated by using spray deposition method. Among the edible oils, soybean oil was chosen for the experiment because it is the most widely used edible oil. Changes of conductivity of the sensor was measured at room temperature and compared with the acid value of the oxidized oil samples. The acid value is the amount of carboxylic acids found in an edible oil, which is an indicator of the degree of oxidation found in an edible oil.

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II. Experimental

A. Fabrication of a SWNT sensor

Au/Ti electrodes were deposited onto glass (0.7mm thick) substrates by the using shadow mask and E-beam evaporation methods. 30nm thick Ti, used for an adhesion layer, was first deposited and then a subsequent 200nm thick Au layer was deposited. 1mg of HIPCO SWNTs (85% purity, purchased from Unidym, inc. USA) were ultrasonicated for 2 hours in 30ml of Dimethylformamide (DMF) (Purchased from Sigma-Aldrich CO. Ltd.) in order to disperse the SWNTs. The DMF solution forms a suspension. This suspension was then ultracentrifuged for 10 minutes at 5000 rpm in order to remove the SWNT bundles and improve the dispersion quality. A hotplate was heated to 160□ to evaporate the DMF as soon as the suspension was sprayed onto to the prefabricated electrode substrates. Thus a SWNT thin film was formed on the electrode. After that, the fabricated SWNT sensor was dried at room temperature for 2 days in order to stabilize the channel resistance before the experiment was conducted.

B. Preparation of oil samples

Seven soybean oil samples, each one at a different acid value, were prepared in the laboratory in order to investigate the change of the electrical conductivity of the SWNT sensor when the acid value of the oil increases. In order to oxidize the new oil, we fried several food in the oil at 180℃ . Each oil samples' acid value was measured using the titration method. The acid values of the oxidized soybean oil samples were 0 (new oil), 0.33, 1.19, 1.75, 2.38, 3.03, and 3.67 (mgKOH/g). The acid value of the edible oils increases as the oils get more oxidized.

C. Measurements

Seven SWNT sensors were prepared to measure the soybean oil samples. In order to minimize any variable that could affect the sensing test, the measurement of the seven samples was conducted simultaneously in the laboratory. In order to measure the resistance change of the SWNT sensors, a Fluke, which has the capability to measure the response of several sensors simultaneously, was used. First, seven oil samples in seven test tubes were prepared and seven SWNT sensors were connected to the Fluke. Then SWNT sensors were left for 30 minutes in order to stabilize the sensors in ambient conditions. When the SWNT sensors were being stabilized, their resistance kept decreasing slightly. Generally SWNTs behave as p-type semiconductors, so oxygen, an electron donating material in CNTs, supplies electrons to the SWNTs and therefore their conductivity increases[10]. After that, the SWNT sensors were immersed into the oxidized soybean oil samples and the resistance changes of the SWNT sensors was measured.

III. Results and discussion

Figure 1 shows the plot of the resistance change in the SWNT sensors over time. In this study, the response of the sensors is represented as a resistance change ratio, $S(\%) = [(R_f - R_i)] / R_i(\%)$. It is shown that resistance of the SWNT sensors increases rapidly in response to all of the edible oils. The reason for this resistance increase in the sensors is due to the triglycerides, which are the main ingredient of edible oils. As the oil contacts the channel of the SWNT random network, the triglycerides are absorbed by the SWNTs causing a decrease in the electrical conductivity of the sensor through scattering[11] and charge transfer mechanisms[3]. The scattering mechanism, not known clearly until now, increases the resistance of the SWNT, which is caused by the carrier scattering in the SWNT channel due to the contact with the material. However, the scattering mechanism is not the major reason for the response of the sensors. A simple experiment was conducted to compare the effects of the scattering and the charge transfer mechanisms.

Figure 2 shows the response of a SWNT sensor reacting to heptane and hexanal. As represented in the graph, the response of the SWNT sensor to the hexanal dramatically increased, whereas the response to the heptane shows very slight change when compared to the hexanal. This result suggests that the charge transfer mechanism contributes more to the resistance change of the sensors than the scattering mechanism.

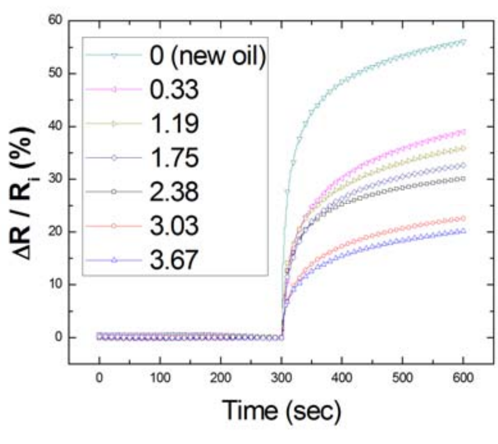

Fig.1 The responses of the SWNT sensors at different oxidation levels.

Therefore, it is clear that the triglycerides in soybean oil act as electron-donating material to the SWNT channel, seeing that the sensor's response to the new oil increased.

Figure 3 is obtained by plotting the values obtained after 1 minute against the acid value. As the acid value of the oils increases, the response of sensors decreases. This behavior definitely shows that the response of the sensors is closely related to the acid value, which is representative of the oxidation level of oils. In order to analyze Figure 5, one needs to know the oxidation process of edible oils. As mentioned above, the main component of new edible oils is triglyceride. At high temperatures, the TAGs decompose to form unsaturated free fatty acids, diglycerides and monoglycerides through hydrolysis[8]. These unsaturated free fatty acids then absorb one hydrogen and two oxygen atoms forming hydroperoxides (the first oxidation product). This first edible oil oxidation product is very unstable in a high temperature environment. Therefore, as the oxidation process progresses, the hydroperoxides decompose into secondary oxidation products, such as carboxylic acids, ketones, alcohols, aldehydes, and hydrocarbons[12]; these organic chemicals change the response of the SWNT sensor.

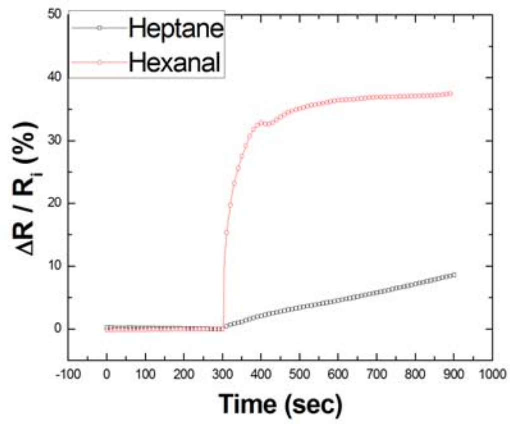

Fig. 2 The comparison of the responses of the SWNT sensor to heptane and hexanal.

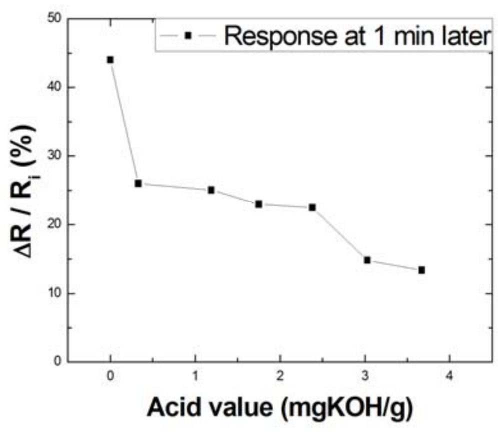

Fig. 3 The response of the SWNT sensors after immersing for 1 minute.

As shown in Figure 3, the response of the sensor for each oxidized oil are relatively small in comparison to the response of the new oil sample. It has been reported that in the primary stage of oxidation, the TAGs decompose faster than they do in the later stages of the oxidation process[13]. Therefore, it can be explained that in the case of the sensor's response to the new oil sample, the large response of the sensor is due to the TAGs which are absorbed by the SWNT channel and due to the donating electrons the conductivity of the channel decreases. As the oil oxidizes, the TAGs decompose rapidly and therefore the adsorption of the TAGs decreases. As shown in Figure 5, the sensor response to the new oil is relatively larger than that of the oxidized oil with the acid value of 0.33. Unlike the TAGs, the secondary oxidation products produced through oxidation are absorbed into the channel. As shown in Figure 3, these organic products also increase the resistance of the sensor, however, this is not true in the case of the TAGs.

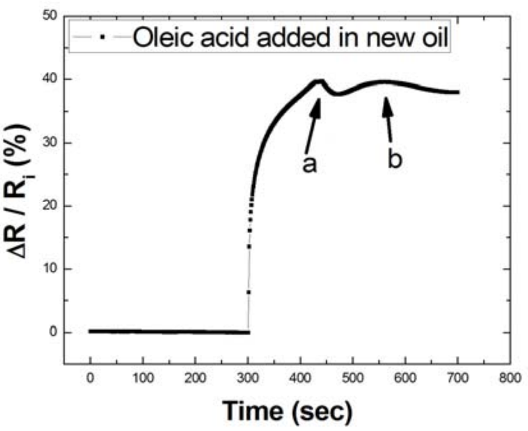

Fig. 4 The response of the SWNT sensor in new oil with the addition of oleic acid.

It is therefore concluded that the secondary oxidation products contain materials that withdraw electrons from the SWNT channel and this causes a decrease in the response of the sensor. The secondary oxidation products of the oils are mainly polar compounds that have functional groups, such as acids(-COOH), ketones(-C=O), alcohols(-OH), and aldehydes(-CHO). The SWNTs used in this study were acid-treated (85% pure), therefore they also have functional groups[14]. The interaction of these functional groups causes a charge transfer between the SWNTs and the organic chemicals. Among these chemicals, oleic acid, a carboxylic acid, was tested to confirm the decrease in the response of the sensor. The SWNT sensor was immersed in 25mL of new oil and oleic acid was added. In order to disperse the oleic acid in the new oil, the solution was stirred. Figure 4 shows the effect of the oleic acid on the resistance of the sensor in new oil.When 100μL of oleic acid was added, the response of the sensor decreased slightly. The result shows the electron withdrawing effect of oleic acid. However, the response of the sensor increased again because the TAGs may interrupt the reaction of the functional group of the oleic acid and the channel. 100μL of oleic acid was further added; the response of the sensor decreased as predicted. However the response time was slightly longer. This may be due to the TAGs and the oleic acid which already occupy the contact sites of the channel, resulting in the reaction time for the second response to be extended. This result shows the TAGs' strong electron donating characteristics and the acid group's electron withdrawing effect.

IV. Conclusion

The electrical characteristics of SWNT sensors in oxidized edible oils at different oxidation levels were investigated. The response of the SWNT sensors decreased as the acid value of the edible oils increased. The main sensing mechanism is the charge transfer between the oil components and the SWNT channel. As oil oxidizes, the TAGs, which are electron donating materials, decompose and various organic chemicals are produced. New oil contains many TAGs which causes the channel conductance to be low. However, oxidized edible oil has a lower TAG concentration and have a higher concentration of the decomposed products. Therefore, the electron donating effect caused by the TAGs weakens and the secondary oxidation products become the primary component that influences the conductivity of the channel. These organic chemicals have different functional groups, such as carboxylic acid, alcohol, aldehydes, and ketones; each functional group donates or withdraws electrons to the channel. It can be concluded that the electron withdrawing materials from the decomposition of TAGs make the conductivity of the channel relatively higher. Consequently, this sensor can determine the condition of edible oils by the difference in the responses of the SWNT sensors. The manufacturing process of the sensors is simple, therefore it can be readily commercialized. Although only soybean oils were tested in this paper, the components of different types of edible oils are so similar that this result can be easily applied to other edible oils.

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References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56–58.
[2] J. Kong, NR Franklin, C. Zhou, MG Chapline, S. Peng, K. Cho, and H. Dai, Nanotube molecular wires as chemical sensors, Science 287 (2000) 622-625.
[3] J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han and M. Meyyappan, Carbon Nanotube Sensors for Gas and Organic Vapor Detection, Nano Letters 3 (2003) 929-933.
[4] PW Barone, S. Baik, DA Heller, MS Strano, Near-infrared optical sensors based on single-walled carbon nanotubes, Nat. Mater. 4 (2005) 86-92.
[5] Q. Zhao, Z. Gan, Q. Zhuang, Electrochemical Sensors Based on Carbon Nanotubes, Electroanalysis 14 (2002) 1609-1613.

[6] FT Orthoefer, Care of food service frying oils, J. Am. Oil Chem. Soc. 65 (1988) 1417-1419.

[7] T. Yasukawa, K. Yasunaga, Nutritional functions of dietary diacylglycerols, J. Oleo Sci. 50 (2001) 427-432.

[8] C. W. Fritsch, Measurements of frying fat deterioration: a brief review, J. Am. Oil Chem. Soc. 58 (1981) 272-274.

[9] K. Robards, A. F. Kerr, E. Patsalides, Rancidity and its measurement in edible oils and snack foods. A review, Analyst 113 (1988) 213-224.

[10] Seung-Hoon Jhi, Steven G. Louie, and Marvin L. Cohen, Electronic Properties of Oxidized Carbon Nanotubes, Phys. Rev. Lett. 85 (2000) 1710-1713.

[11] Zsolt E. Horváth, Antal A. Koós, Krisztián Kertész, György Molnár, Gábor Vértesy, Márton C. Bein, Tamás Frigyes, Zoltán Mészáros, József Gyulai, László P. Biró, The role of defects in chemical sensing properties of carbon nanotube films, Appl. Phys. A-Mater. Sci. Process. 93 (2008) 495-504.

[12] E. N. FRANKEL, Lipid peroxidation, Prog. Lipid Res. 19 (1980) 1-22.

[13] Felix A. Aladedunye, Roman Przybylski, Degradation and Nutritional Quality Changes of Oil During Frying, J. Am. Oil Chem. Soc. 86 (2009) 149-156.

[14] Jian Chen, Mark A. Hamon, Hui Hu, Yongsheng Chen, Apparao M. Rao, Peter C. Eklund, Robert C. Haddon, Solution Properties of Single-Walled Carbon Nanotubes Science 282 (1998) 95-98.