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SWNT Sensors for Monitoring the Oxidation of Edible Oils

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Abstract

Several methods are available to measure the oxidation of edible oils, such as their acid, peroxide, and anisidine values. However, these methods 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 study, an edible oil-condition sensor was fabricated using single-walled nanotubes (SWNTs) made using the spray deposition method. SWNTs were dispersed in a dimethylformamide solution. The suspension was then sprayed using a spray gun onto a prefabricated Au/Ti electrode. To test the sensor, oxidized edible oils, each with a different acid value, were prepared. The SWNT sensors were immersed into these oxidized oils, and the resistance changes in the sensors were measured. We found that the conductivity of the sensors decreased as the oxidation level of the oil increased. In the case of the virgin oil, the resistance change ratio in the SWNT sensor S(%) = {[(Rf – Ri)]/Ri}(%) was more than 40% after immersion for 1 min. However, in the case of the oxidized oil, the resistance change ratio decreased to less than that of the response of the virgin oil. This result suggests that the change in 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, Acid value, Chemical sensor

1. INTRODUCTION

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

Edible oils such as soybean or corn oils are among the most widely used food sources and are essential to our food culture. However, when the oils are used repeatedly, undesirable oxidation products of edible oils are generated, some of which may cause health problems [6]. The principal components of edible oils are triglycerides (TAGs) [7], an ester that consists of a glycerol backbone combined with three fatty acids. When edible oils are used, the TAGs are decomposed into organic compounds harmful to human health because of the hydrolysis mechanism [8]. Consequently, repeatedly monitoring used oils is very important to ensure that they are still viable. Many methods are available to determine the degree of oxidation in edible oils, such as their acid, peroxide, or anisidine value [9]. However, these methods are time consuming and inconvenient; thus, developing a more convenient and time-saving method is necessary.

In this work, a sensor that uses SWNTs to detect the degradation of edible oils was fabricated. As stated above, the oxidation of edible oils generates organic compounds such as aldehydes, alcohols, hydrocarbons, and carboxylic acids. These oxidation materials are absorbed by the SWNT and change the conductivity of the SWNT channels via charge-transfer mechanism [3]. The SWNT oil-condition sensor was fabricated using the spray deposition method. Among the edible oils, soybean oil was chosen for the experiment because it is the most widely used edible oil. The changes in the conductivity of the sensor were 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 edible oil, which indicates the degree of oxidation in the edible oil.

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2. EXPERIMENTAL

2.1 Fabrication of SWNT sensor

Au/Ti electrodes were deposited onto glass (0.7-mm thick) substrates using the shadow mask and E-beam evaporation methods. A 30-nm-thick Ti, used as an adhesion layer, was first deposited, and a 200-nm-thick Au layer was subsequently deposited. 1 mg of HIPCO SWNTs (85% purity, purchased from Unidym, Inc., USA) was ultrasonicated for 2 h in a 30-ml of dimethylformamide (DMF) (purchased from Sigma-Aldrich Co., Ltd.) to disperse the SWNTs. The DMF solution formed a suspension, which was then ultracentrifuged for 10 min at 5000 r/min to remove the SWNT bundles and to improve the dispersion quality. A hotplate was heated to 160 °… to evaporate the DMF as soon as the suspension was sprayed onto the prefabricated electrode substrates. Thus, an SWNT thin film was formed on the electrode. Thereafter, the fabricated SWNT sensor was dried at room temperature for 2 days to stabilize the channel resistance before the experiment was conducted. Figure 1 shows the fabricated SWNT sensor (8 mm × 4 mm) and the schematic structure of the sensor.

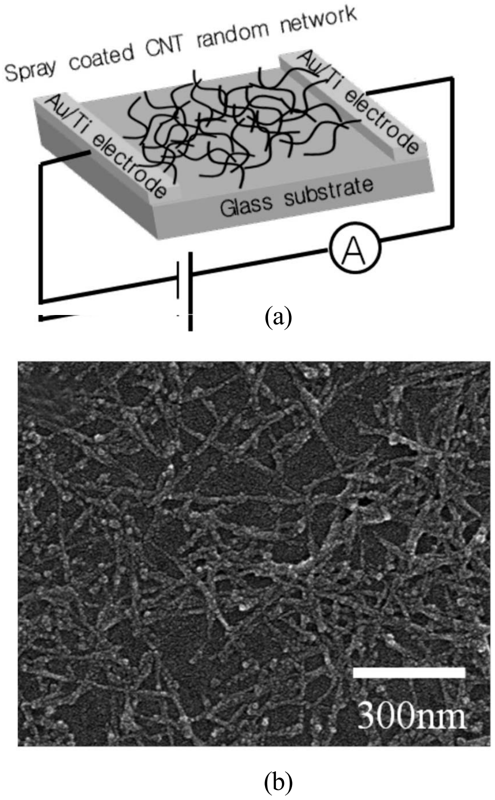

Fig. 1. (a) Schematic of the SWNT sensor and (b) SEM image of the SWNT random network.

2.2 Preparation of oil samples

Seven soybean oil samples, each with a different acid value, were prepared in the laboratory to investigate the change in the electrical conductivity of the SWNT sensor when the acid value of the oil increases. To oxidize the virgin oil, we fried several foods in the oil at 180℃. Each oil sample's acid value was measured by the titration method. The acid values of the oxidized soybean oil samples were 0 (virgin oil), 0.33, 1.19, 1.75, 2.38, 3.03, and 3.67 mg KOH/g. The acid value of the edible oils increased as the oils became more oxidized. Figure 2 shows the different oxidized soybean oil samples.

Fig. 2. Image of the oxidized soybean oil samples, from the left: virgin oil, 0.33, 1.19, 1.75, 2.38, 3.03, 3.67 mg KOH/g.

2.3 Measurements

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

3. RESULTS AND DISCUSSIONS

Figure 3 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, i.e., S(%) = {[(Rf / Ri)]/Ri}(%). We have shown that the resistance of the SWNT sensors increases rapidly in response to all the edible oils because of the TAGs, which are the main ingredients of edible oils. As the oil makes contact with the channel of the SWNT random network, the TAGs are absorbed by the SWNTs, resulting in 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.

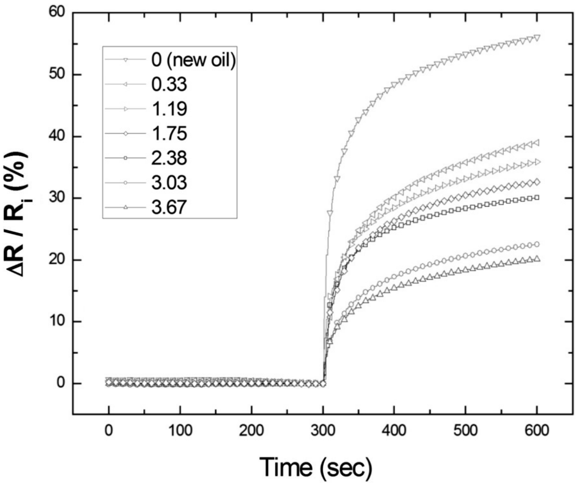

Fig. 3. Responses of the SWNT sensors at different oxidation levels.

Figure 4 shows the response of the SWNT sensor reacting to heptane and hexanal. As represented in the graph, the response of the SWNT sensor to the hexanal dramatically increased whereas that to the heptane shows a very slight change. This result suggests that the charge-transfer mechanism contributes more to the resistance change in the sensors than to the scattering mechanism. Therefore, it is clear that the TAGs in the soybean oil act as the electron-donating materials to the SWNT channel from the observation that the sensor's response to the virgin oil increased.

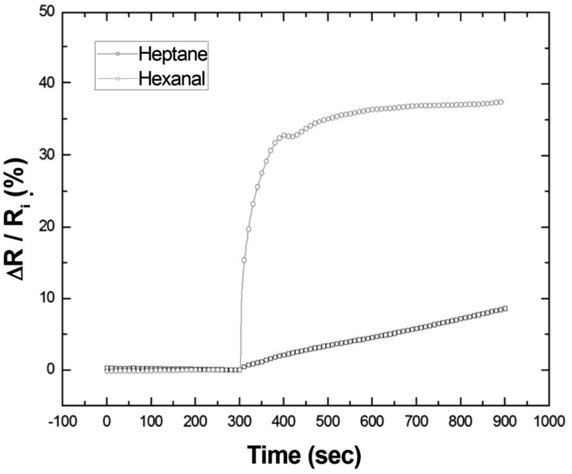

Fig. 4. Comparison of the responses of the SWNT sensor to heptane and hexanal.

Figure 5 shows the plot of the values obtained after 1 min against the acid value. As the acid value of the oils increases, the response of the 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 the oils. To analyze Figure 5, we must know the oxidation process of edible oils. As mentioned earlier, the main component of virgin edible oils is the TAG. At high temperature, 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.

Figure 5 shows that the responses of the sensor for each oxidized oil are relatively small in comparison with that of the virgin oil sample. It has been reported that TAGs decompose faster in the primary stage of oxidation than in the latter stages [13]. Therefore, we can explain that the sensor's large response to the virgin oil sample is due to the TAGs (which are absorbed by the SWNT channel) and the donating electrons; thus, the channel conductivity decreases. As the oil oxidizes, TAGs decompose rapidly, and therefore, the adsorption of TAGs decreases. Figure 5 shows that the sensor response to the virgin oil is relatively larger than that to the oxidized oil with an acid value of 0.33.

Unlike the TAGs, the secondary oxidation products are absorbed by the channel. Figure 5 shows that these organic products also increase the resistance of the sensor.

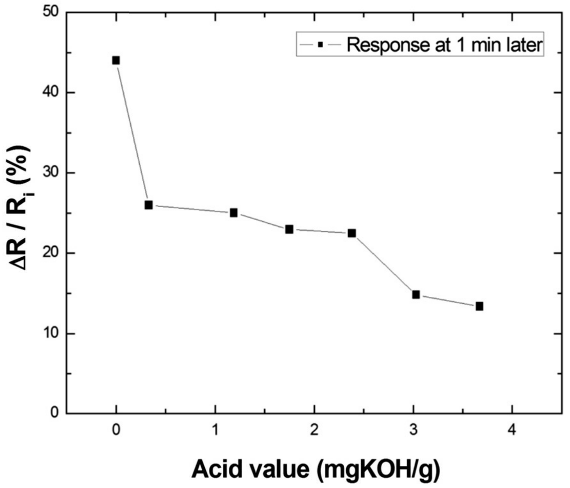

Fig. 5. Response of the SWNT sensors after immersion for 1 min.

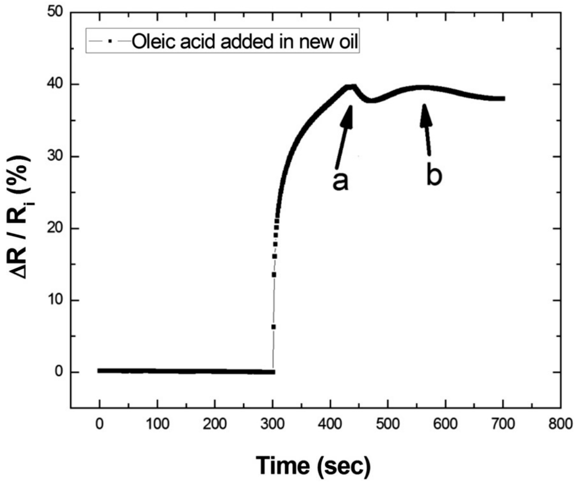

Fig. 6. Response of the SWNT sensor in virgin oil with the addition of oleic acid.

However, this condition is not true in the case of the TAGs. We can therefore conclude that the secondary oxidation products contain materials that withdraw electrons from the SWNT channel, and this process 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 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 25 mL of virgin oil, and oleic acid was added. To disperse oleic acid in virgin oil, the solution was stirred. Figure 6 shows the effect of oleic acid on the resistance of the sensor in virgin oil. When 100 μL of oleic acid was added, the response of the sensor decreased slightly (point a in Figure 6). The result shows the electron-withdrawing effect of oleic acid. However, the response of the sensor increased again (point b in Figure 6) because the TAGs may have interrupted the reaction of the functional group of oleic acid and the channel. Another 100 μL of oleic acid was added; the response of the sensor decreased as predicted. However, the response time was slightly longer, which may be because the TAGs and oleic acid already occupied the contact sites of the channel, resulting in the extension of the reaction time of the second response. This result shows the TAGs' strong electron-donating characteristics and the acid group's electron-withdrawing effect.

4. CONCLUSIONS

The electrical characteristics of SWNT sensors in oxidized edible oils at different oxidation levels have been investigated. The response of the SWNT sensors decreased as the acid value of the edible oils increased. In the case of virgin oil, the resistance change ratio of the SWNT sensor, i.e., $S(\%) = \{[(R_f-R_i)]/R_i\}(\%)$, was more than 40% after immersion for 1 min. However, in the case of oxidized oil, the resistance change ratio decreased to less than that of the response of virgin oil. 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. Virgin oil contains many TAGs, which causes the channel conductance to become low. However, oxidized edible oil has a lower TAG concentration and has 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 components that influence 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. We can conclude 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 study, the components of different types of edible oils are very similar. Therefore, this result can be easily applied to other edible oils.

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