

Polyethylenimine Coated Carbon Nanotube for Detecting Rancidity in Frying Oil

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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 which 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 in ambient air without the need of heating or UV exposure.

Keywords—Carbon nanotubes, polyethylenimine, sensor, oxidized oil

I. 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 to 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 volatilize 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 compounds 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 have a rapid recovery time, making them suitable detection devices that can be deployed for quality control in the food industry. Free fatty acid value will be used in this report as a gauge for the oxidation level of our oil samples and to measure the accuracy of our sensors.

II. EXPERIMENTAL

A. Sensors

1mg of purified HIPCO SWCNTs, purchased from Unidym, were dispersed in 30 ml of N,N-dimethylformamide and bath sonicated for 4 hours. The dispersion was then centrifuged at 15,000 rpm for 15 minutes; only the top 20% of the dispersion was collected in order to reduce the number of SWCNT bundles. Previous works [7,8] 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. For enhancing the sensitivity and to impart selectivity to the sensors, we adsorbed polyethylenimine (PEI), purchased from Sigma Aldrich, onto the SWCNT network. A solution of 20wt% PEI/methanol was

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prepared and the sensors were immersed for 2 hours 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 minutes in order to evaporate the methanol from the surface, leaving behind only the PEI coated SWCNT thin film.

B. Oil Samples

A common household soybean oil was purchased and heated in a silicon bath at temperatures of $180 \pm 5^\circ\text{C}$ 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 obtained. Oils with an acid value of 2.0 mg KOH/g and above are no longer suitable for consumption and need to be discarded. 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.

C. Measurements

5ml of each oil sample at room temperature was placed into test tubes and the sensors were immersed into each sample in an ascending order based on their acid values. The sensors were first immersed into the oil and then left to recover in ambient conditions at an interval of 5 minutes. The change in resistance was measured with a constant bias of 1 V using a Keithley 2400 Sourcemeter.

III. RESULTS AND DISCUSSION

Experiments were first carried out to study the effects of the oil oxidation level on as-purchased purified SWCNTs. Fig. 1 shows the response of the sensor and its partial recovery curve. Initially, the resistance increased as the sensor was first immersed into the new oil sample and continued to do so even after extracting the sensor from the sample. The known mechanisms which could cause such an increase in resistance are the carrier scattering introduced by the polymer chains [1] and the donor effect of the chemical functional groups found in the oil sample. After the first immersion, the resistance of the sensor continued to decrease as the sensor was immersed in oil samples with higher acid values. In order to confirm this descending trend, 3 sensors were immersed in each oil sample and the average resistance changes were measured (Fig. 1 inset). The results coincide with our first observations; this trend is most probably attributed to the increase in the amount of acceptor molecules, such as free fatty acids, produced as the oil oxidizes. Acids act as electron acceptors, causing the resistance of the p-type SWCNT channel to decrease [9]. 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.

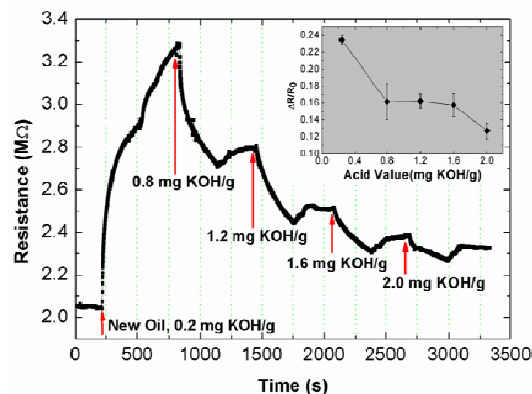


Fig. 1 Continuous response of the untreated SWCNT sensor immersed in oxidized oil samples with acid values from 0.2 to 2.0 mg KOH/g. The inset shows the average response of the untreated SWCNT sensors for each acid value. For each measurement, a different sensor was used to observe the consistency in the trend.

In order to improve the recovery of these sensors, the surface of the thin film SWCNT has to be chemically treated. Pengfei Qi *et al.* reported that PEI functionalized SWCNTs 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 thorough 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 [10].

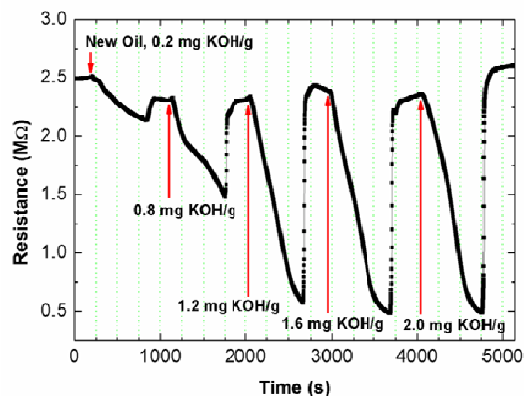


Fig. 2 Response of a single PEI functionalized SWCNT sensor immersed for 5 (a) and later 10 (b) minutes in the oxidized oil samples. The recovery of the sensor was carried out in room temperature air.

Fig. 2 shows the response of the PEI functionalized SWCNT sensor towards the oxidized oil samples after 10 minutes of immersion, respectively. 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 full rapid recovery 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 [11]. The PEI basically acts as an intermediate charge transfer layer from the SWCNT to the electron acceptors.

In previous reports [10,11,12], 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 minutes, 1, 2 and 12 hours. The sensors submerged for 10 minutes 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 hours of immersion, both sensors were selective and recoverable at the same time, and little difference in the response magnitude between the sensors was recorded. 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. Strong 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 hours. However, 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 [11]. 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 and the response magnitude of the sensors (Table I). At a low SWCNT density (Fig. 3(a)), the response towards the oxidized oil was almost undetectable. The SWCNT network is near the threshold percolation and thus the overall resistance is dominated by the

tube-tube or bundle-bundle contact resistance [13]. Even if the

TABLE I SUMMARY OF THE RECOVERABILITY AND RESPONSE OF SENSORS WITH DIFFERENT SWCNT NETWORK DENSITIES

SWCNT network density	Low	Medium	High
Initial resistance after immersion in PEI (Ω) \square	~20M	~2M	~10K
Recovery	No	Yes	No
Response Magnitude	Large	Large	Small

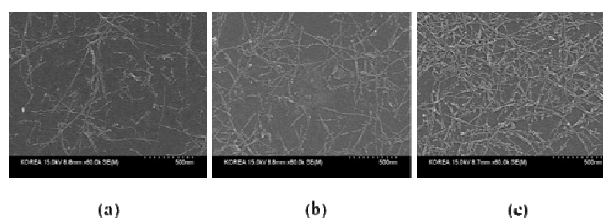


Fig. 5 Scanning electron microscope images of the (a) low, (b) medium, and (c) high density SWCNT network.

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. 3(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. 3(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.

IV. 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 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.

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