The Effects of Exfoliated Graphite Concentration on Sensing Properties of Chitosan/Exfoliated Graphite Film Crosslinked with Glutaraldehyde

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Abstract: In this study, chitosan/exfoliated graphite (CEG) sensors were used for formaldehyde detection in various concentration i.e. 1 ppm; 1,5 ppm; 2 ppm; 5 ppm; and 10 ppm. The sensors were fabricated using electrodeposition method to form film sensors. The cross-linking agent is glutaraldehyde, it was used to enhance the life time of CEG film sensors. The effect of exfoliated graphite concentration on sensing properties of CEG film sensors has been proven by improvement on response and sensitivity of sensors when the concentration of EG increased. Formaldehyde solution was dropped onto chitosan/EG film sensor and the response of the chitosan/EG film sensors toward formaldehyde was recorded as output voltage. The measurement result of maximum output voltage from chitosan/EG film sensors is greater than chitosan sensors for 10 ppm formaldehyde. Increasing on concentration of formaldehyde made the output voltage of the sensors increased.

1 INTRODUCTION

The control on utilization of formalin by goverment is weak (Noordiana, 2011). Formalin is a forbidden food as stated in The Food Regulation. According to WHO standards in 2002, the maximum formalin content contained in food was 1 mg/l equivalent to 1 ppm (WHO, 2002).

Chitosan is biopolymer which produced by treating seafood waste and it functions as an attractive sensitive material. Chitosan easily can be modified to be used as an effective sensitive material due to modification of the chitosan structure, excellent film-forming ability, adhesive, high heat stability (Yang, 2013). The high solubility in acidic media makes chitosan easily deposited onto a substrate to form film (Sun, 2011). The use of thin films of chitosan continues to expand in various industries such as industrial biotechnology,. environmental, agricultural industries etc. (Majety, 2000). The advantages of non-porous film layers offer high selectivity, permeability and mechanical strength (Kanti, 2004).

Graphite is produced naturally or synthetically. Graphite is a crystalline carbon which is highly conductive (with an electrical conductivity of 10^4 S/cm). Graphite's derivative called exfoliated graphite or expanded graphite could be a filler for producing conductive materials. The electrical conductivity of exfoliated graphite is high. Exfoliated graphite has a good affinity for organic compounds (Debelak, 2007). Neat graphite (NG) can be converted to intercalated or expandable graphite through chemical oxidation in the presence of concentrated acid such as H_2SO_4 or HNO_3. Expanded graphite is then obtained by exfoliation and expansion of graphite by heating in a furnace above 600^{o}C (Demitri, 2015). Surface area and bulk density essentially affect the physicochemical and physical properties of carbon materials. Exfoliated graphite can be also synthesized from graphite oxide (OG) (Buchsteiner, 2006).

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Most of current techniques to detect fomaldehyde are sophisticated equipment, expensive and time consuming. So, it is highly desirable to develop a sensitive and easy-to-use method for formaldehyde detection.

2 MATERIALS AND METHOD

2.1 Materials and Instruments

Materials used in this research are chitosan powder supplied by Sigma–Aldrich (medium molecular weight), graphite, glutaraldehyde, CH_3COOH 2%, $H_2SO_{4(p)}$, $HNO_{3(p)}$, $CoCl_2$ 0,01 M, KSCN 1 M and HCl 2 N (Merck).

Oven, Furnace, hot plate, magnetic stirrer, printed circuit board (PCB), centrifuge, an ultrasonic, a set of FTIR Shimadzu IR prestige-21 and a set of XRD Shimadzu XRD-6100 were used as tools to perform the material preparation and material characterization.

2.2 Preparation of Chitosan Solution

Chitosan powder was dissolved in acetic acid 2% then stirred using a magnetic bar for 24 hours at room temperature to prepare the chitosan gel.

2.3 Preparation of Exfoliated Graphite

Exfoliated graphite was prepared using graphite and it was mixed with nitric and sulfuric acid for 24 hours. Then, it became intercalated graphite. The mixture was filtered and washed until the pH became neutral. Exfoliated graphite was dried in an oven. Then the intercalated graphite compound was subjected thermal shock to temperatures of 900^{o}C.

2.4 Preparation of Chitosan/Exfoliated Graphite Solution

Exfoliated graphite 400 mg was added into chitosan solution and stirred for 1 hour then sonicated. After that, the solution was centrifuged 5000 rpm to collect supernatant solution for chitosan/EG film sensors fabrication.

2.5 Preparation of Chitosan/Exfoliated Graphite (EG) Film Sensor

Chitosan/exfoliated graphite film sensors were made by chitosan/EG solution using electrodeposition method. The substrate of the sensor used is a printed circuit board (PCB). The electrodeposition process is illustrated as in Figure 1. The supplied voltage was fixed at 2,5 volts. Then it left to dry for 5 minutes at 105^{o}C in an vacuum oven. Chitosan/EG films were cross-linked using glutaraldehyde 25%. $CoCl_2$ 0,01 M was used as a template to protect amine groups. KSCN 1 M is a solution to remove the template and HCl 2 N was used to ensure the template is completely removed. Formaldehyde solution was varied into 1 ppm; 1,5 ppm; 2 ppm; 5 ppm; and 10 ppm. Formaldehyde solution was dropped onto chitosan/EG film sensors and it was detected by amperometric method. The output voltage was displayed based on the characteristic of the film sensor. The response of the sensor towards formaldehyde was recorded as output voltage.

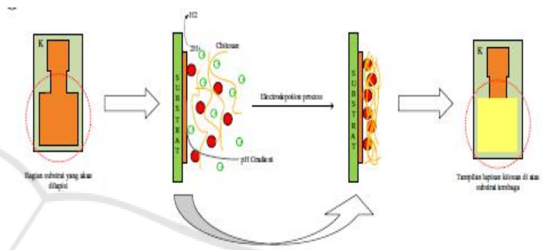

Figure 1. Electrodeposition Process of Chitosan/EG film sensor.

3 RESULTS AND DISCUSSION

Chitosan would assemble onto the PCB surface when it is positively charged in acidic conditions to form chitosan sensor. Exfoliated graphite was found improving the sensitivity of chitosan film sensor. The addition of glutaraldehyde as crosslinking agent improved the lifetime of chitosan/EG. The output of chitosan/EG sensors was in the potential voltage. Chitosan/EG film sensors showed good sensitivity and long lifetime in measurement with various concentration of formaldehyde. The measurements were repeated three times. The output voltage of chitosan/EG film sensors when detecting formaldehyde are reported in Table 1.

Table 1 shows the output voltage of chitosan/EG film sensors when the sensor's surface was exposed to formaldehyde with various concentration. The output voltage of the sensor indicates the sensitivity of chitosan/EG film sensor during detecting various concentration of formaldehyde. The output voltage values were within the range of 0,421 V to 0,589 V for 1-10 ppm of formaldehyde. The highest output voltage (0,589 V) was observed when chitosan/EG film sensor exposed to 10 ppm formaldehyde, while the lowest output voltage (0,421 V) was observed at 1 ppm formaldehyde. If it is compared to chitosan sensor which gave output voltage 0.143 V when the sensor was exposed to 1 ppm of formaldehyde. As shown by the table, increasing concentration of formaldehyde shows the increasing of output voltage.

Table 1**:** The output voltage of crosslinked chitosan/EG film sensor towards formaldehyde.

Formaldehyde Concentration (ppm)	Average of Output Voltage (V)
1	0,421
1,5	0,434
2	0,447
5	0,504
10	0,589

FTIR studies confirmed the successful of crosslinking of chitosan and chitosan/EG with glutaraldehyde as displayed in Figure 2. The peak at 1072,42 cm^{-1} shows stretching vibration of –C-O- from chitosan and glutaraldehyde. The absorption band at the wave number 1651,07 cm^{-1} is the O=C-N group which proves that exfoliated graphite binds to chitosan. Wave number of 1118.71 cm^{-1} is a stretching of C-O-C bridge which proves cross-linkage between chitosan/EG and glutaraldehyde.

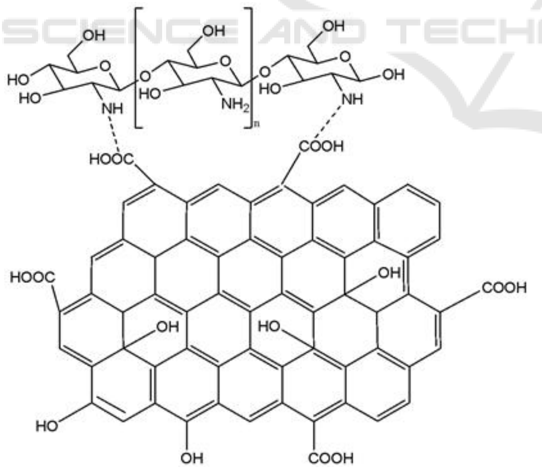

Figure 2: The FTIR spectrum of chitosan, chitosan/EG, crosslinked chitosan and crosslinked chitosan/EG films.

The interaction between exfoliated graphite and chitosan formed hydrogen bonding between carboxylic acid of exfoliated graphite and amine group of chitosan. The illustration of the reaction can be seen in Figure 3.

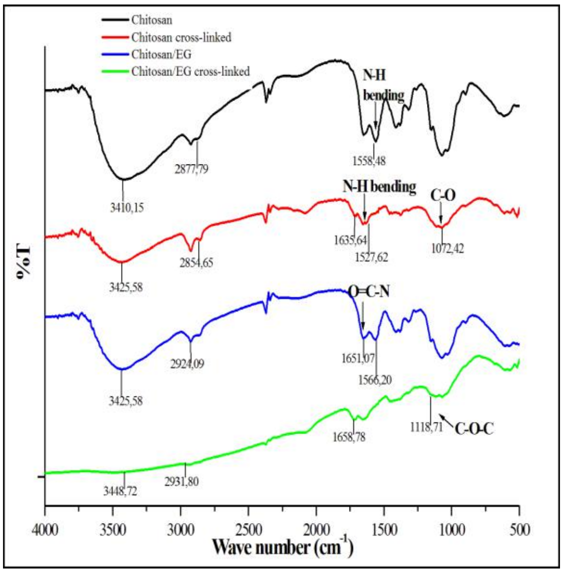

Figure 3: Reaction between chitosan and exfoliated graphite

The XRD patterns of graphite and exfoliated graphite are represented in Figure 4. Based on XRD analysis, the diffraction angles of the graphite forms peak at 26,530^o with d-spacing 3,3571 Å while the diffraction angles of exfoliated graphite forms peak at 26,588^o with d-spacing 3,4524 Å. It proved that there was an expansion of the lattice of exfoliated graphite thus exfoliated graphite was obtained in a greater d-spacing value than graphite.

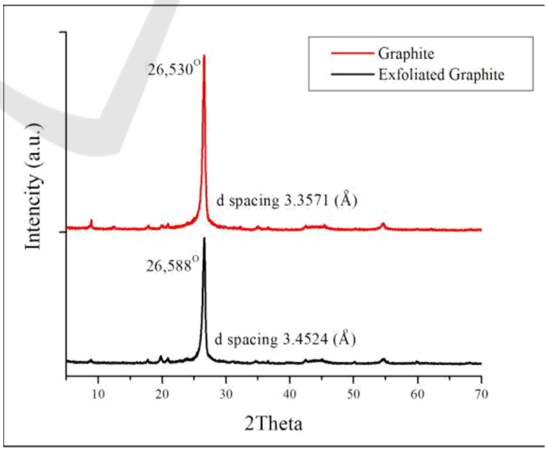

Figure 4: XRD of graphite and exfoliated graphite

4 CONCLUSIONS

The electrical testing results of chitosan/EG film sensors showed that chitosan/EG film sensor was potentially capable to detect formaldehyde in various concentration of formaldehyde. The sensitivity of chitosan/EG film sensors has been proven by the different output voltage values when the sensors exposed to different concentration of formaldehyde. Increasing concentration of formaldehyde indicated the increasing on output voltage. The highest output value (0,589 V) was recorded during detecting 10 ppm of formaldehyde, while the lowest value (0,4217 V) for 1 ppm of formaldehyde. The cross-linking process of chitosan with glutaraldehyde has been successfully done and it has been proved by FT-IR spectrum. The crosslinking improved the lifetime f the sensors.

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