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The effect of ferredoxin in enhancing the sensing properties of chitosan based acetone sensors

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Abstract. The purpose of this study is to investigate the effect of ferredoxin on sensing properties of chitosan-based acetone sensors. The composites were facilely prepared and their sensing properties toward low concentration of acetone have been investigated at room temperature. The improvement of electrical and physical conditions of the sensors has been successfully carried out by blending ferredoxin into chitosan solution for fabrication of ferredoxin-chitosan based acetone sensors. Electrochemical deposition method has been chosen to fabricate the sensors. The ratio of ferredoxin to chitosan was varied at 5:95, 10:90, 15:85 and 20:80. The sensors were exposed to acetone vapour with acetone concentrations of 0.1, 1, 10, 20, 50, and 100 ppm. Among the sensors, 15\% ferredoxin-chitosan based acetone sensor exhibited the highest response. The response of the sensor is higher 20\% than chitosan-based acetone sensors. The surface roughness of sensor was smoother compared to that of chitosan-based acetone sensors.

1. Introduction
Chitosan which is a natural polymer possesses film forming characteristic. When pKa value of chitosan solution is \(~6.5\), the chitosan can be soluble in aqueous acidic media [1] and can be electrochemically deposited on to a metal plate to fabricate film sensors. In our previous report, the chitosan-based acetone sensors (CBASs) have been used to detect the low concentration acetone [2]. Research on acetone sensor is very interesting because shows a great potential for an application of diabetes mellitus diagnosis through the exhaled breath [3-4]. The concentration of acetone in breath varies from 0.3 to 0.9 ppm for healthy individuals [5]. While the acetone concentration in the exhaled breath of diabetic patients was reported to be more than 1.8 ppm [6]. The difference enabling this acetone sensor as a suitable disease biomarker in detecting diabetes [5-7].
It has been proved that CBASs have good acetone sensing properties including fast response, good stability, recovery, repeatability and reproducibility [2]. However, the CBAS performance still can be further improved. Some researchers have blended the chitosan with other polymeric compounds such as cellulose, polypyrrole, polyaniline and rice starch or blending chitosan with metal oxides such as iron oxide and zinc oxide [8]. However, there is no report of using ferredoxin as a mixture of chitosan in order to enhance the sensing properties of chitosan film.

Ferredoxin appears to be huge promising as a bio-mixture because apart from natural reproducible resource, being compound which contains iron-sulfur proteins and represented as [2Fe-2S]2+. When the ferredoxin is in reduced state, one electron is transferred to the specific iron atom which results in the [2Fe-2S]2+ cluster becomes the reduced [2Fe-2S]+ cluster by releasing one electron. Whereas, in the oxidized state of ferredoxin, one of these two iron atoms accept an electron and both iron atoms are in a similar chemical state [9-10]. Thus, the presence of ferredoxin in CBASs can enhance the electrical conductivity and in turns, it increases the sensitivity of CBASs when exposed to the certain absorbates.

The changes in output electrical signal of the Fdx-CBASs toward different concentration acetone vapor were compared to that of CBASs to clarify the effect of ferredoxin to electrical properties of CBAS. Fdx-CBAS properties including response, stability, recovery, repeatability and reproducibility were investigated at room temperature. The experimental results were used to determine the sensing mechanism of the sensors.

2. Experimental

Chitosan powder (Sigma Aldrich, practical grade) with deacetylation degree 75-80% was used as a sensing material. Ferredoxin was purchased from Sigma Aldrich and has been used as mixture of chitosan. The ratio of ferredoxin to chitosan solution was varied at 5:95, 10:90, 15:85 and 20:80, respectively. The chitosan solution was prepared by following procedure described by Nasution et al. (2013) [2]. The aqueous chitosan solution was prepared by stirring chitosan in 1.75% of acetic acid because it can only be soluble in water when protonated in acidic solutions. At low pH, chitosan becomes a cationic polyelectrolyte [11].

Initially, chitosan, ferredoxin, and chitosan-ferredoxin blend were characterized using FTIR (Perkin Elmer). For the process of aluminum patterning on silicon wafer, it was fabricated by following the process flow illustrated by Nasution et al. (2012) [2], which the main steps included a cleaning process, oxidation, metallization and photolithography. The chitosan solution was electrochemically deposited onto the aluminum surface. The chitosan’s amines become deprotonated at pH 6.5 [11]. Therefore, the chitosan loses its charge and forms an insoluble deposit on the cathode surface [2]. When the chitosan solution was blended with ferredoxin, the amino group will attract the FeS to form a chemical bond as described in the following reaction:

\[
\text{Chitosan-NH}_3^+ \cdot \text{FeS} + \text{OH}^- \rightarrow \text{Chitosan-NH}_2 \cdot \text{FeS} + \text{H}_2\text{O} \]

The electrical measurement of sensor properties was carried out using a setup. Each Fdx-CBAS was tested by placing it into a testing chamber which equipped with flexible positive and negative contacts. Right and left sides of Fdx-CBAS surface were connected to the contacts to flow electrical current. The output signals were interfaced to a personal computer through a data acquisition system (DAQ) (National Instrument 6008). LabVIEW was used to control data acquisition applications to automatically display and record the measured output voltages of ferredoxin-CBAS.

In this work, the acetone vapor for different concentrations (0.1, 1, 10, 20, 50 and 100 ppm) was exposed to the sensor surface continuously. Each acetone with certain concentration was placed into a small container. By controlling the open and close of inlet and outlet valves, the procedure to do the
ceaseless expose can be explained as follows. The first, chitosan film sensor was exposed with 0.1 ppm acetone vapor for 5 minutes and directly followed by the dry air exposure for 5 minutes for sensor recovery. Once the recovery completed, the sensor was again exposed with 1 ppm acetone vapor for 5 minutes without a deferment and then followed by the second recovery using dry air. This procedure was repeated for 10, 20, 50 and 100 ppm consecutively. The data was continuously collected at every 30 seconds. The output signals were measured on two terminals of load resistor because it functioned as a protector to avoid the damage of DAQ system if the overload or short current occurs. The sensor response values are calculated as the ratio \((R_g - R_a)/R_a \times 100\%\) where \(R_g\) and \(R_a\) are the electrical resistance values of the sensor in the mixture acetone gas/wet air and in normal air, respectively.

3. Results and discussion

Chitosan contains two important functional groups in its molecular structure; they are amine (NH\(_2\)) group and hydroxyl (OH) group [12]. The amine group has lone pair electrons which act as an active site. In this case, the amine group interacted with acetone vapor contaminated wet air to provide the output signals of CBAS and 15\% Fdx-CBAS, respectively. Therefore, it is very important to prove the existence of amine and hydroxyl groups in CBAS using a FTIR. The FTIR spectrum was obtained by scanning the chitosan film using spectrometer (Perkin Elmer). The existence of amine and hydroxyl groups was evidenced by the absorption peaks at 3271.04 cm\(^{-1}\) and 2919.15 cm\(^{-1}\) for chitosan film (Fig. 1a) and at 3269.45 cm\(^{-1}\) and 2918.08 cm\(^{-1}\) for ferredoxin-chitosan film (Fig.1b), which are associated with overlapping of NH\(_2\) and OH, respectively [12-13]. While, the existence of ferredoxin [Fe-S] in 15\% ferredoxin-chitosan film is shown by extra peaks which they appear at 1999 cm\(^{-1}\) and 2194 cm\(^{-1}\) [14]. Based on two graphs, blending 15\% ferredoxin into chitosan solution has not change the basic molecular structure of chitosan.

The Fdx-CBAS surface which is smoother compared to the CBAS surface may be due to the bonding formation between ferrum of ferredoxin and amine groups of chitosan. It is believed that the bonding makes the whole composite structure becomes more compact because the ferrum elements occupy the empty spaces in the chitosan matrix. In addition, it was observed that the appearance of bubbles on Al surface due to hydrogen gas formation during the electrochemical deposition of chitosan solution reduced significantly after ferredoxin being blended. The existence of the bubbles resulted in uneven sensor surface after annealing process.
Figure 1. Infrared spectra of (a) chitosan film and (b) ferredoxin-chitosan film

The electrical characteristics of Fdx-CBAS fabricated from different ratio of ferredoxin were tested to wet air to select the best composition of blend film. The resistance as a function of time is presented in Fig. 2. In this case, the testing for each Fdx-CBAS was repeated five times continuously. It was found that the blending of ferredoxin into chitosan solution at the ratio of 5:95 resulted in the reduction of CBAS resistance when exposed to wet air. It can be clearly seen that 5% ferredoxin blended CBAS is lower than CBAS. By making higher ratio of ferredoxin to chitosan solution at 10:90, there was a significant resistance reduction effect wherein the resistance of 10%Fdx-CBAS is ~64% lower than CBAS. When the ratio increased to 15:85, the resistance of sensor is still decreasing significantly. Nevertheless, at the ratio of 20:80, the maximum resistance of Fdx-CBAS decreased in very small difference compared to that of 15:85. Besides that, Fig. 2 shows also that in general, the Fdx-CBASs for all compositions can work in fast response, good stability, complete recovery and good repeatability. Even though 20%Fdx-CBAS resistance is a bit lower than 15%ferredoxin-CBAS but it was found that 20%Fdx-CBAS has sensitive layer which sticked weaker on the aluminum layer than 15%Fdx-CBAS. Hence, Fdx-CBAS made from the ratio of ferredoxin to chitosan at 15:85 are the most suitable blend for sensor fabrication. Then the electrical properties of 15%Fdx-CBAS were compared to CBAS to evidence the improvement of CBAS performance.
Figure 2. Comparison of output electrical signals of Fdx-CBAS exposed to wet air.

Figure 3 shows the electrical response of CBAS and 15%Fdx-CBAS exposed to acetone vapour as well as the changes in humidity and ambient temperature during the testing. The response time of CBAS is the initial time which required by CBAS to sense the presence of the target molecules on its surface approximately 10 s for each concentration. The variations of acetone concentration are 0.1, 1, 10, 20, 50 and 100 ppm, respectively. The sensor response values were calculated by the formula as in our previous report [2]. It was exhibited that the electrical response values of 15%Fdx-CBAS were higher almost 20% for all acetone concentrations compared to those of CBAS. In this case, the calibration curves of CBAS and 15%Fdx-CBAS that describe the increase in response to acetone concentration is shown in Fig. 3. The linear increases in response for both CBAS and 15%Fdx-CBAS start from the acetone concentration in range of 10-50 ppm with the correlation coefficient values for CBAS and 15%Fdx-CBAS are 0.9716 and 0.9548, respectively. Below 10 ppm, both CBAS and 15%Fdx-CBAS showed the sharp response, while above 50 ppm their response was slow.
As expressed in some reports [15], the sensing mechanism starts when the chemisorbed oxygen on the sensor surface traps the electrons in conduction band and forms the oxygen species \( \text{O}_2^- \) and \( \text{O}^- \). During exposure of CBAS to water molecules \((\text{H}_2\text{O})\), the water molecules create surface tension on the chitosan film. The existence of surface tension compels the electrons to escape from the trap of oxygen species and this reconverts the oxygen species to oxygen gas as described by the Eq. (2) [2].

\[
\text{Chit-NH}_2 + 2\text{O}^- + \text{H}_2\text{O} \rightarrow \text{Chit-NH}_2 + \text{O}_2 + \text{H}_2\text{O} + 2e^- .............................................(2)
\]

Besides that, it was illustrated that the hydrogen atoms of the amino groups bind with the oxygen of water molecules to form hydrogen bonds and provide an electrical pathway or bridge for free electrons to transfer from one particle to another. When the chitosan solution was blended with ferredoxin, the nucleopilic chitosan which contains lone pair electrons bound readily with ferredoxin \([2\text{Fe-2S}]^{2+}\). When the ferredoxin \([2\text{Fe-2S}]^{2+}\) presents in chitosan film structure and makes CBAS more conductive. The proposed chemical reaction is described by the Eq. 3.

\[
\text{Chit-NH}_2\text{-FeS} + 2\text{O}^- + \text{H}_2\text{O} \rightarrow \text{Chit-NH}_2\text{-FeS} + \text{O}_2 + \text{H}_2\text{O} + 2e^- .............................................(3)
\]

When the 15\%Fdx-CBAS was exposed to water molecules, much more free electrons move randomly through the hydrogen bonding. And when acetone vapor molecules exist in exposed air, as in our previous report the acetone vapor molecules which have an inherent molecular vibration "stirs up" the water molecules, to break the surface tension and makes water molecules is easier to be vaporized. The vaporization of water molecules will lessen the existence of electrical pathway or bridge [2]. It has been
predicted that the effect of blending has resulted in the band gap of 15% Fdx-CBAS narrower, so that the electrical response of 15% Fdx-CBAS is higher than that of CBAS for all acetone vapor concentrations.

4. Conclusion
The ferredoxin was successfully exploited as a novel mixture to improve electrical properties of CBAS. The improvements were indicated by higher electrical response of Fdx-CBAS than that of CBAS. Therefore, Fdx-CBASs have a bigger potential to be applied as breath acetone detectors to diagnose the diabetics. This will lead to faster realization to create a painless and steadfast detection technique for early diabetes detection.

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