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Enhancement of the Sensing Properties of Chitosan Films as an Acetone Gas Sensor with the Addition of Tin Oxide (SnO_2)

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ABSTRACT

In this study, the sensing properties of the chitosan film sensor were successfully improved by adding tin oxide (SnO_2). The addition of SnO_2 concentration to the chitosan solution was 0.01%, 0.05%, 0.1%, and 0.5% (w/v). The sensor is fabricated as a film using the electrodeposition method. The sensing properties of chitosan and chitosan-SnO_2 film sensors were exposed to acetone gas with concentrations of 0.5; 1; 1.5; 2; 2.5; and 3 ppm. The testing results show that chitosan film's response and repeatability properties produced the highest output voltage of 514 mV at 1.5 ppm, while the lowest output voltage value was 499.72 at 0.5 ppm. The addition of SnO_2 with the highest concentration of 0.5% increased the response and repeatability properties in the form of the highest output voltage to 569.34 mV at 3 ppm, while the SnO_2 concentration of 0.01% resulted in the lowest sensor output voltage of 504.84 mV at 0.5 ppm. The reproducibility of chitosan film became better due to the addition of SnO_2, which resulted in a low STDEV value of 0.005 compared to that of chitosan film without the addition of SnO_2, namely 0.156. The sensitivity of the chitosan film added by SnO_2 increased, indicated by the increase in the slope value of 17.142 compared to the chitosan film without the addition of SnO_2, which was 1.82. The SEM characterization showed that adding SnO_2 increased the number of pores formed on the film, which strengthened the ability to absorb acetone. This is also evidenced by the FTIR results, which show the presence of SnO_2 in the peak range of the wavenumbers from 677-717 cm^{-1}. Therefore, the chitosan film sensor with the addition of SnO_2 concentration showed better-sensing properties than chitosan film, which could be applied as an acetone gas sensor.

Keywords: Acetone, Chitosan Film, Electrodeposition, SnO_2

ABSTRAK

Dalam penelitian ini, sifat-sifat penginderaan sensor film kitosan telah berhasil ditingkatkan dengan menambahkan bahan Tin Oxide (SnO_2). Konsentrasi penambahan SnO_2 pada larutan kitosan yaitu 0,01%, 0,05% 0,1% dan 0,5% (w/v). Sensor difabrikasi dalam bentuk film menggunakan metode elektrodeposisi. Pengujian sifat-sifat penginderaan sensor film kitosan dan kitosan-SnO_2 dilakukan dengan mengekspos gas aseton dengan konsentarsi 0,5; 1; 1,5; 2; 2,5 dan 3 ppm. Hasil pengujian sifat respon dan pengulangan menunjukkan film kitosan menghasilkan tegangan keluaran tertinggi sebesar 514 mV pada 1,5 ppm sedangkan nilai tegangan keluaran terendah sebesar 499,72 pada 0,5 ppm. Penambahan SnO_2 dengan konsentrasi tertinggi yaitu 0,5% meningkatkan sifat respon dan pengulangan berupa tegangan keluaran tertinggi menjadi 569,34 mV pada 3 ppm sedangkan konsentrasi SnO_2 0,01% menghasilkan tegangan keluaran sensor terendah sebesar 504,84 mV pada 0,5 ppm. Sifat respodusibilitas film kitosan menjadi lebih baik akibat penambahan SnO_2 dengan menghasilkan nilai % STDEV yang rendah yaitu 0,005 dibandingkan film kitosan tanpa penambahan SnO_2 yaitu 0,156. Sifat sensitivitas film kitosan yang ditambahkan SnO_2 mengalami peningkatan yang ditandai dengan meningkatnya nilai slope sebesar 17,142 dibandingkan film kitosan tanpa penambahan SnO_2 yaitu 1,82. Hasil

karakterisasi SEM menunjukkan penambahan SnO_2 meningkatkan banyaknya pori yang terbentuk pada film yang memperkuat kemampuan dalam menyerap aseton. Hal ini juga dibuktikan oleh hasil FTIR yang menunjukkan keberadaan SnO_2 pada rentang puncak pita serapan 677-717 cm^{-1}. Oleh karena itu, sensor film kitosan dengan konsentrasi penambahan SnO_2 menunjukkan sifat-sifat penginderaan yang lebih baik dibandingkan film kitosan sehingga memiliki potensi untuk diaplikasikan sebagai sensor gas aseton.

Kata kunci: Aseton, Elektrodeposisi, Film Kitosan, SnO_2

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1. Introduction

Diabetes is a chronic disease that has become a significant health issue [1]. A person can develop diabetes due to a lack of insulin production or improper use of insulin in the body. Diabetes mellitus is not a disease that can be cured but can only be controlled to prevent worsening conditions. Therefore, prevention and early detection of diabetes mellitus are appropriate and necessary steps to reduce the high prevalence of diabetes.

One of the volatile organic compounds (VOCs), acetone, has been recognized as a significant biomarker of diabetes mellitus, and acetone detection can enhance diagnostic accuracy [2],[3]. A person is indicated to have diabetes when the concentration of acetone gas exhaled through breath exceeds 1.8 ppm, which is associated with normal glucose metabolism and carbohydrate digestion [2].

Acetone sensors have been developed using various materials and forms with relatively good performance. One of the natural alternative materials used to detect acetone gas is chitosan [4]. Chitosan is a biopolymer widely used in biosensor applications due to its biocompatibility, biodegradability, non-toxicity, non-immunogenicity, excellent film-forming ability with good adhesion, strong mechanical properties, higher permeability, and cost-effectiveness [5]. Chitosan has functional groups such as hydroxyl (OH) and amine (NH_2), which are essential in reacting with acetone. However, previous studies were conducted using voltage input, and the performance of chitosan as an acetone sensor still exhibited a low response range and decreasing repeatability, necessitating improvement.

To enhance the sensing properties such as response, repeatability, reproducibility, and sensitivity of the chitosan film sensor for acetone gas at low concentration ranges, the addition of metal oxide material, namely tin oxide (SnO_2), can be employed. Tin oxide (SnO_2) is a semiconductor material with an optical band gap in the range of 3.40 - 4.75 eV, an isoelectric point (IEP ~ 5.0), and higher conductivity compared to TiO_2 and SiO_2, and has been applied in microelectronics, optoelectronics, solar cells, and gas sensors [6].

2. Material and Methods

2.1. Materials

Chitosan, with a deacetylation degree of 85%, is produced by Sigma Aldrich. Tin oxide powder with a molecular weight of 150.71 is produced by Fluka Chemical. Glacial acetic acid 100%, distilled water, and acetone 98% are made by EMD Millipore.

2.2. Fabrication of Chitosan and Chitosan-SnO_2 Films

The chitosan solution was prepared by dissolving 1.75 g of chitosan in 100 mL of 2% (v/v) acetic acid. The chitosan solution was stirred using a magnetic stirrer at 300 rpm for 24 hours at room temperature. For preparing the chitosan-SnO_2 solution, a 1.75% (w/v) chitosan solution was first prepared and stirred for 2 hours. Then, SnO_2 powder was added with varying masses of 0.01 g, 0.05 g, 0.1 g, and 0.5 g for concentrations of 0.01%, 0.05%, 0.1%, and 0.5% (w/v) respectively. The mixture was then stirred using a magnetic stirrer at 300 rpm for 24 hours at room temperature, followed by sonication of the chitosan- SnO_2 solution for 4 hours [7].

The fabrication of chitosan and chitosan-SnO_2 films was then carried out using an electrodeposition process. The electrodeposition process involved immersing two substrates into a container filled with an electrolyte solution, which in this study was the chitosan solution and the chitosan-SnO_2 solution. The coating process requires a voltage source to be applied to the anode and cathode. The cations in the solution moved toward the cathode, while the anions moved toward the anode [8]. After deposition, the films were dried in a vacuum oven at 105°C for 30 minutes.

2.3. Characterization and Testing of the Film

The fabrication resulted in chitosan and chitosan-SnO_2 film sensors with concentrations of 0.01%, 0.05%, 0.1%, and 0.5%. In the next stage, each fabricated sensor sample will be characterized using SEM to reveal the surface morphology of the films and FTIR to analyze the functional groups of the formed films.

The sensing properties of the films were tested by placing the chitosan and chitosan-SnO_2 films at each concentration variation in a test chamber. In this test, the chitosan and chitosan-SnO_2 film sensors were connected to two electrodes: a positive electrode and a negative electrode. These electrodes were then attached to an Arduino Uno-based electronic data acquisition system. The test data was displayed on a computer screen using PLX-DAQ software. The acetone gas used in the testing was derived from liquid acetone, which had been converted into ppm units, and the acetone concentrations varied were 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 2.5 ppm, and 3 ppm.

The testing was conducted by exposing the acetone gas for 3 minutes in the test chamber, as illustrated in Figure 1 (a). For repeatability testing, the sensor must be recovered to restore its initial value by exposing it to dry air from silica gel for 2 to 3 minutes. This was done to equalize the initial values of each composition variation, allowing the differences in response values from the same starting point to be observed. This process is illustrated in Figure 1 (b). The sensing properties tested included response, repeatability, reproducibility, and sensitivity.

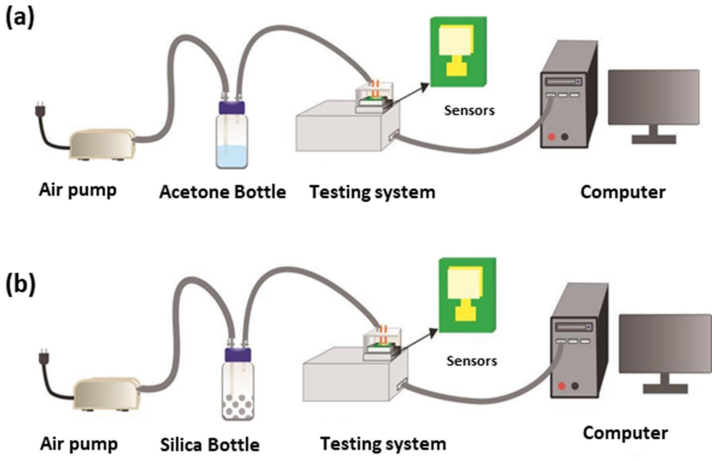

Figure 1. Illustration of sensor testing against (a) acetone gas and (b) sensor recovery with silica gel.

3. Results and Discussion

3.1. Fabrication Film Results

This electrodeposition technique attracts the tertiary amine group (NH_3^+), forming a film layer on the opposing substrate (cathode) (Figure 2). Chitosan dissolved in an acidic solution (low pH) results in the protonation of chitosan into a cationic polyelectrolyte:

$$CHIT\text{-}NH_2\text{-}OH + H_3O^+ \rightarrow CHIT\text{-}NH_3^+\text{-}OH + H_2O \quad (1)$$

When SnO_2 is added, the resulting reaction forms intermolecular hydrogen bonds between SnO_2 and the hydroxyl group (OH):

$$CHIT\text{-}NH_3^+\text{-}OH + H_2O + SnO_2 \rightarrow CHIT\text{-}NH_3^+\text{-}OH\text{- - - }SnO_2 + H_2O \quad (2)$$

When the electrodes (anode and cathode) are immersed in the chitosan solution and an electric current is applied, it produces negative hydroxyl ions:

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

These negative hydroxyl ions (OH^-) are distributed and increase the pH on the electrode surface. The increased pH causes the amine group to deprotonate, resulting in chitosan adhering to the cathode surface and forming a chitosan film layer:

$$CHIT\text{-}NH_3^+\text{- }OH\text{- - - }SnO_2 + OH^- \rightarrow Chit\text{-}NH_2\text{ - }OH\text{- - - }SnO_2 + H_2O \quad (4)$$

The SnO_2 in the chitosan solution is also deposited as a film on the substrate due to the hydrogen bonds formed between SnO_2 and the hydroxyl groups of chitosan.

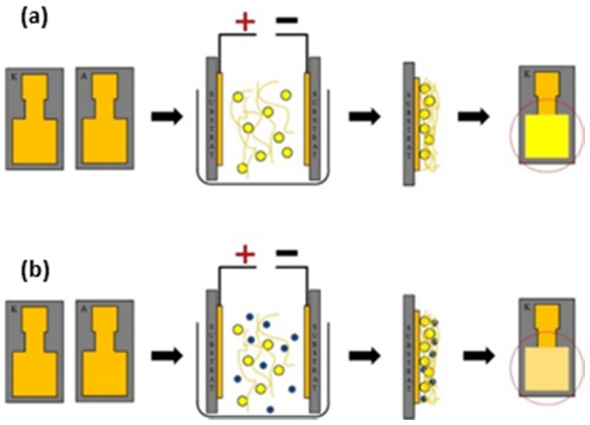

Figure 2. Electrodeposition process of (a) chitosan and (b) chitosan-SnO_2 films.

3.2. Characterization of Films Results

The SEM results shown in Figure 3 (a) indicate a smooth chitosan film surface with minor aggregation. This surface condition changes after the addition of SnO_2, as noted in the presence of white particles on the film surface. This is confirmed by the increase in white particles as the SnO_2 concentration in the chitosan solution rises from 0.01% to 0.5%, as shown in Figures 3 (b-e). This is supported by EDX results, which show increased Sn content with atomic percentages of 10.11%, 17.26%, 18.10%, and 20.09% for SnO_2 concentrations of 0.01%, 0.05%, 0.1%, and 0.5%, respectively.

Pore formation is also observed on the film surface as the SnO_2 concentration increases. This can be seen in the addition of SnO_2 at a concentration of 0.01% in Figure 3 (b), where tiny pores are formed, while at a concentration of 0.5% in Figure 3 (e), the pores are more pronounced and larger. The pore increase is due to electrostatic interactions between chitosan and SnO_2 on the film surface [7]. This pore formation is also evidenced by EDX results, which show an increase in oxygen content with atomic percentages of 33.92%, 40.11%, 44.86%, 50.43%, and 51.62% for chitosan films and chitosan with SnO_2 concentrations of 0.01%, 0.05%, 0.1%, and 0.5%, respectively.

The pores formed on the film can help acetone molecules enter and interact with the chitosan amine groups on the film, leading to assumed high sensitivity values. Additionally, larger pores on the film surface can result in more excellent absorption, allowing the film to swell more quickly when exposed to acetone gas, potentially affecting the sensor's repeatability.

Furthermore, it can be observed that the chitosan film with added SnO_2 has a wider particle distribution compared to the chitosan film alone. This indicates that the film enhances electron transfer between particles, producing higher response values or output voltage. The SEM characterization images demonstrate the presence of SnO_2 in the chitosan film sensor.

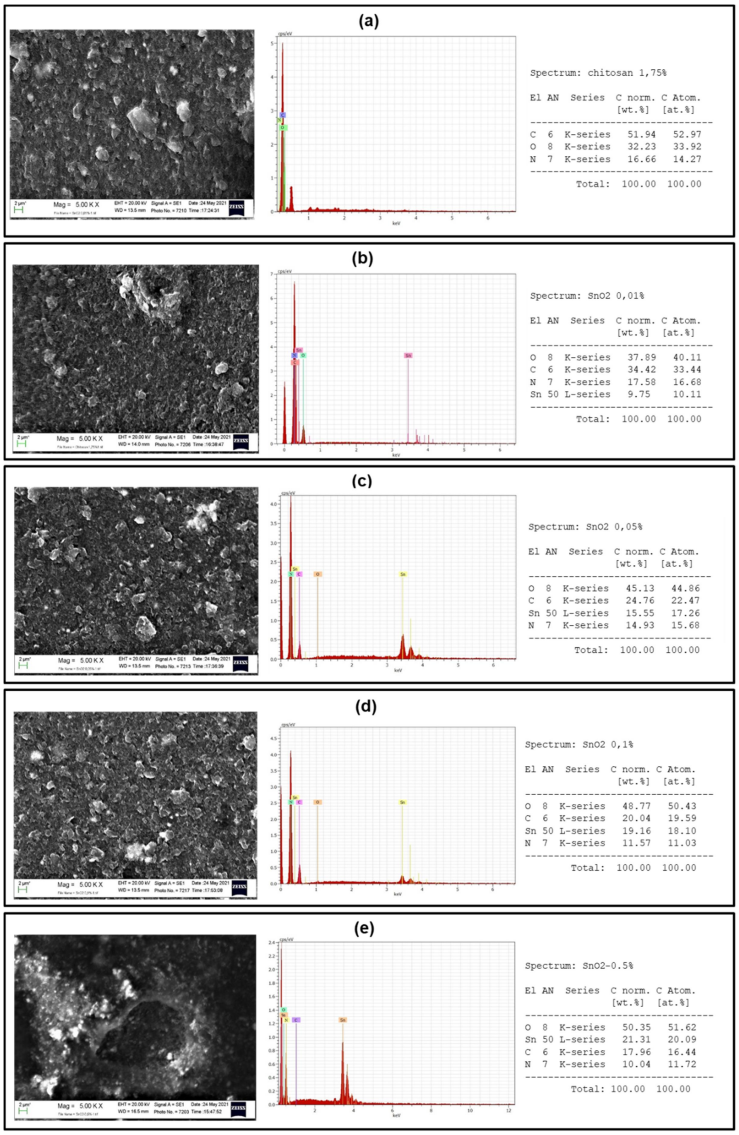

Figure 3. Surface morphology characterization results of (a) chitosan film, (b) chitosan-0.01% SnO_2, (c) chitosan-0.05% SnO_2, (d) chitosan-0.1% SnO_2, and (e) chitosan-0.5% SnO_2.

Figure 4 shows the FTIR spectra of chitosan and chitosan- SnO_2 films. The FTIR spectrum of the chitosan film shows O-H and N-H stretching at 3536 cm^{-1} and 3302 cm^{-1}. The O-H and N-H bending absorption bands are observed at 1439 cm^{-1} and 1589 cm^{-1}. In addition to these functional groups, C-H and C-N stretching are seen at 2878 cm^{-1} and 1167 cm^{-1}. Peaks at 1126 cm^{-1} and 1043 cm^{-1} indicate C-O-C and C-O stretching absorption bands.

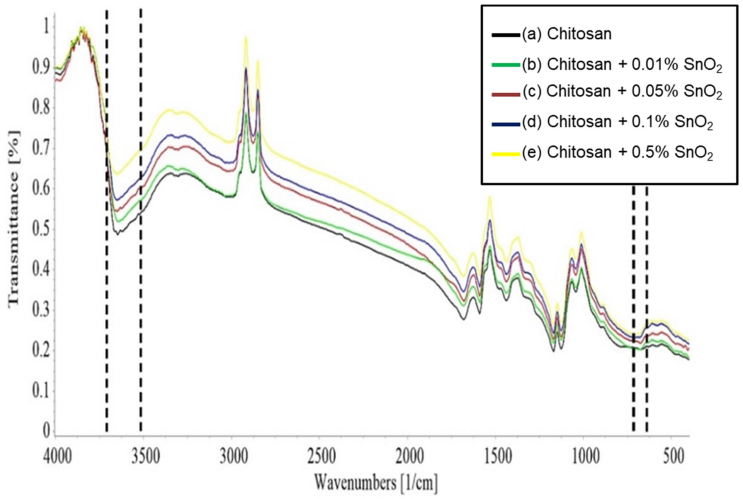

Figure 4. FTIR characterization results of (a) chitosan film, (b) chitosan-0.01% SnO_2, (c) chitosan-0.05% SnO_2, (d) chitosan-0.1% SnO_2, and (e) chitosan-0.5% SnO_2.

3.3. Sensor Testing Results

3.3.1. Response and Repeatability Testing

The sensor testing of chitosan films and chitosan films with added SnO_2 was conducted by exposing the sensor to acetone gas at concentrations of 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 2.5 ppm, and 3 ppm. As seen in the graph in Figure 5 (a), the chitosan film sensor still shows a low response, which can be observed from the sensor's output voltage when exposed to acetone gas, with values of 499.72 mV, 508.22 mV, 514 mV, 506.09 mV, and 505 mV, respectively. The chitosan sensor also shows a decrease in repeatability with a relatively wide range.

In this study, the chitosan film sensor with added SnO_2 showed an increased response as the SnO_2 concentration in the chitosan increased. The sensor's ability to distinguish acetone gas at various concentrations also improved. This is because a higher gas concentration leads to more gas interacting with the sensitive material on the sensor surface, as seen in each graph with the increase in SnO_2 concentration.

The test results also indicated that a 0.5% SnO_2 concentration is optimal for enhancing the film's response when exposed to acetone gas. The increased response is due to the addition of SnO_2, which creates more pores on the film surface, enhancing its absorption capacity for acetone gas. This allows more acetone compounds to interact with the NH groups on the film, as demonstrated in the graph in Figure 5 (e).

Figure 5 also shows the repeatability of each chitosan and chitosan-SnO_2 film sensor in detecting acetone gas. The graph indicates that chitosan films with added SnO_2 have better repeatability than chitosan films alone. However, in the fifth repetition, the sensors with 0.1% and 0.5% SnO_2 start to show a decline in repeatability. This may be due to physical damage to the film, as the large pores on the surface result in higher absorption, making the film more prone to swelling and reducing the sensor's durability when repeatedly exposed to acetone gas.

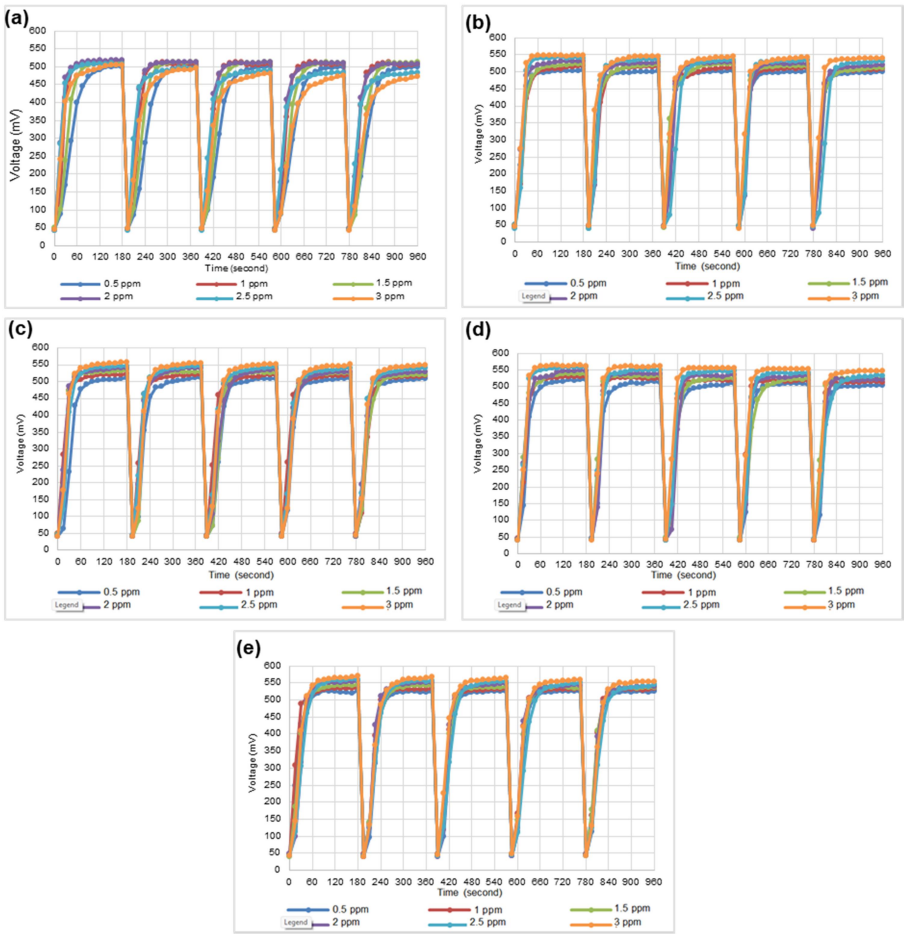

Figure 5. Response and repeatability graphs of (a) chitosan film, (b) chitosan-0.01% SnO_2, (c) chitosan-0.05% SnO_2, (d) chitosan-0.1% SnO_2, and (e) chitosan-0.5% SnO_2.

3.3.2. Reproducibility Test Results

The reproducibility testing of the sensor was conducted by preparing five sensors for each concentration, all with the same composition, and then exposing them to acetone gas at concentrations of 0.5 ppm, 1 ppm, 1.5 ppm, 2 ppm, 2.5 ppm, and 3 ppm. The results showed that the reproducibility of the chitosan film sensors with added SnO_2 is better than that of the chitosan film sensors, as seen in the graph (Figure 6).

This is evidenced by the fact that when the five chitosan-SnO_2 film sensors were exposed to acetone gas, they produced relatively similar maximum output voltages compared to the maximum output voltages of the chitosan film sensors. Among the various concentrations of chitosan-SnO_2, the 0.5% concentration showed the best reproducibility. These results indicate that the electrodeposition method used can fabricate more stable chitosan-SnO_2 film sensors.

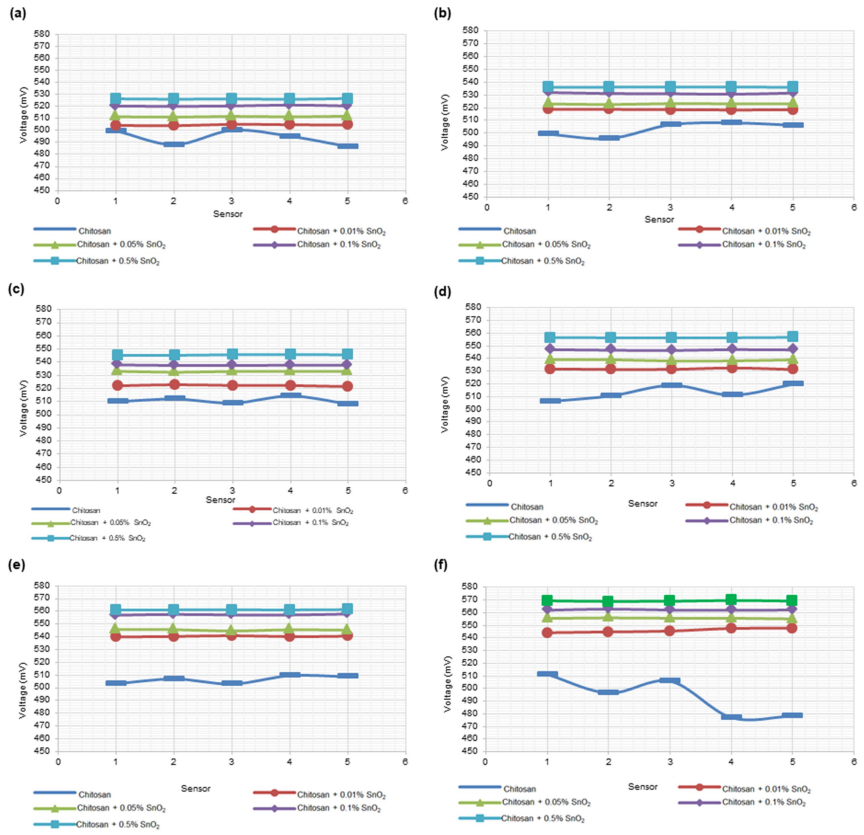

Figure 6. Reproducibility of chitosan film sensors and chitosan-SnO_2 sensors when exposed to acetone gas at concentrations of (a) 0.5 ppm, (b) 1 ppm, (c) 1.5 ppm, (d) 2 ppm, (e) 2.5 ppm, and (f) 3 ppm.

3.3.3. Sensitivity Test Results

As shown in Figure 7, the addition of SnO_2 to the chitosan film has a significant impact on the output of each sensor. The linearity of the measurements improves with increasing SnO_2 concentration. This is evidenced by the increasing sensor output voltage as the amount of acetone gas exposure increases. Figure 7 illustrates that the fabricated chitosan and chitosan-SnO_2 films exhibit good linearity, with values of 0.0645, 0.9867, 0.9877, 0.9902, and 0.9910 for the SnO_2 concentrations of 0%, 0.01%, 0.05%, 0.1%, and 0.5%, respectively.

According to Hejjaji, et al. [9], sensitivity can be calculated based on the slope of the graph that compares the physical quantity given to the sensor output. Figure 7 also shows the sensitivity of the film, as indicated by the slope values of 1.82, 16.525, 17.013, 17.142, and 17.281 for the SnO_2 concentrations of 0%, 0.01%, 0.05%, 0.1%, and 0.5%, respectively. Based on these results, the chitosan-SnO_2 0.5% sensor has the best sensitivity and linearity. These values indicate that the addition of SnO_2 significantly enhances the sensitivity of the chitosan film.

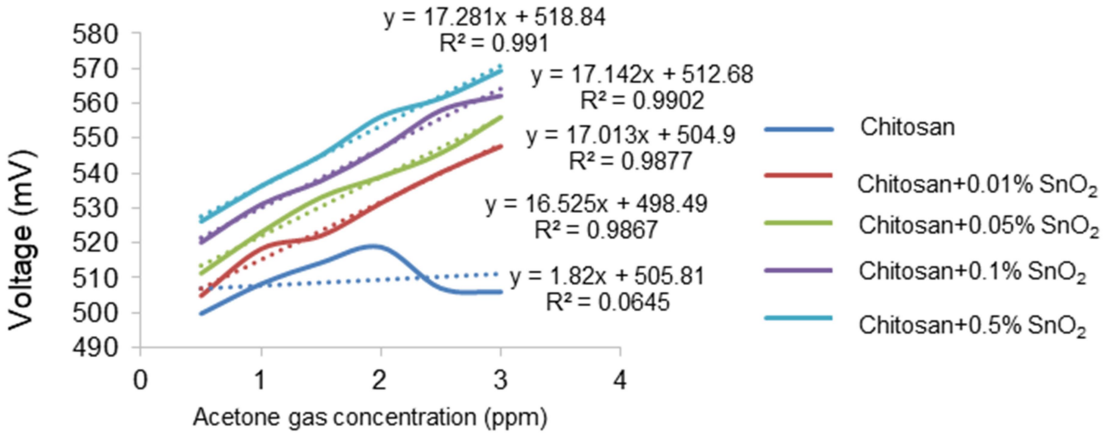

Figure 7. Sensitivity of chitosan film sensors and chitosan-SnO_2 film sensors.

3.4. Sensing Mechanism

Several scientific articles state that the resistance of the sensor is greatly influenced by the chemisorbed oxygen process, which allows the sensor output to be analyzed [4], [10]. In normal air, oxygen molecules are absorbed on the film's surface, trapping free electrons present in the film and forming oxygen species such as O_2^-, O^-, or O_2^- [11], [12]. This absorption process is called chemisorbed oxygen, where a low output voltage is generated when normal air reacts with the film surface. The state of oxygen absorption can be described by the following equations:

$$O_2\,(gas) \rightarrow O_2\,(adsorbed) \quad (5)$$

$$O_2\,(adsorbed) + e^- \rightarrow O_2^- \quad (6)$$

When the film is exposed to acetone, acetone molecules react with the amine functional groups on the film via hydrogen bonding. From a physical perspective, this interaction occurs due to the difference in polarity between the two compounds, as illustrated in Figure 8. This interaction also causes surface tension that forces electrons out of the oxygen species traps. The released electrons move from the valence band to the conduction band, increasing the sensor's output voltage. Based on this analysis, it is evident that the higher the acetone concentration, the higher the output voltage due to the increasing hydrogen bonding. Conversely, when exposed to normal air, the output voltage decreases compared to when exposed to acetone. This happens because the presence of O_2 again traps the electrons, causing the output voltage to drop.

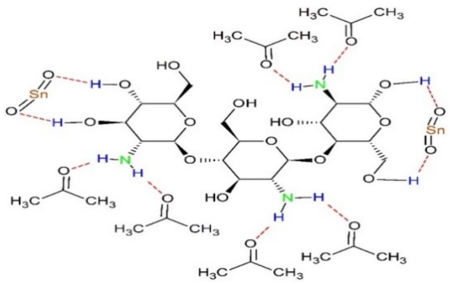

Figure 8. Illustration of hydrogen bonding formed between amine groups and acetone gas molecules.

4. Conclusion

The enhancement of chitosan film properties as an acetone gas sensor by adding tin oxide (SnO_2) has been successfully achieved. The modified chitosan films showed improved response, repeatability, reproducibility, and sensitivity compared to unmodified chitosan films. The 0.5% SnO_2-chitosan film demonstrated a response of 569.34 mV at 3 ppm acetone, good repeatability, consistent reproducibility, and high sensitivity. Surface morphology analysis indicated that higher SnO_2 concentrations resulted in denser, more porous films, facilitating better electron movement and acetone absorption. FTIR analysis confirmed new absorption peaks linked to SnO_2, validating its significant impact on the film's performance. These

findings suggest that SnO_2-enhanced chitosan films have strong potential as acetone gas sensors for diabetes detection due to their ability to detect low acetone concentrations.

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