International Journal of Electrical and Computer Engineering (IJECE)
Vol. 7, No. 3, June 2017, pp. 1154~1160
ISSN: 2088-8708, DOI: 10.11591/ijece.v7i3.pp1154-1160

Improvement on Alcohol Breath-Analyzer Ethanol Biosensor based on Roselle-Chitosan Blend

Ahmed M. S. Eljali[1], Irwana Nainggolan[2], Shahrir Hashim[3], Tulus Ikhsan Nasution[4]
[1,3]Polymer Engineering Department, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81300, Skudai, Johor Bahru, Malaysia
[2]School of Materials Engineering, University Malaysia Perlis, Perlis, Malaysia
[4]Physics Department, Faculty of Mathematic and Natural Science, Universitas Sumatera Utara, Medan 20155, Sumatera Utara, Indonesia

Article Info

Article history:

Received Sep 18, 2016
Revised Nov 6, 2016
Accepted Nov 20, 2016

Keyword:

Biosensor
Breath-analyzer
Chitosan-roselle blend
Ethanol

ABSTRACT

This paper presents a study on designing of a breath-analyzer ethanol biosensor through vaporization technology. A roselle extract and chitosan smart gel were used to fabricate the bio-sensing material. Sol-gel electrochemical deposition method was used to coat a thin film of the sensing material blend on patterned golden surface printed circuit board. Differentiation, response time and repeatability properties were studied by exposing 100ppm, 50ppm and 25ppm of ethanol vapor to the breath-analyzer. The accuracy of the breath-analyzer was tested by using I-V electrical testing. The analyzed data demonstrated that the breath-analyzer ethanol biosensor is capable of identifying the concentration of ethanol vapor at room temperature successfully, which can be used as analyzer of alcohol concentration when the sensor exposed to the exhale breath. The roselle-chitosan film sensors have shown the characteristic of a reliable sensor i.e. good sensitivity, selective, repeatable, able to recover and stable.

Corresponding Author:

Ahmed M. S. Eljali,
Polymer Engineering Department,
Faculty of Chemical Engineering,
Universiti Teknologi Malaysia,
81300, Skudai, Johor Bahru, Malaysia.
Email: ahmed.eljaji2@yahoo.com

1. INTRODUCTION

Intoxication problems such as gas emission and inflammable gas leakages provide the impetus for fundamental and applied research in environmental areas. For the sake of environmental monitoring and control of chemical processes, many efforts to develop simple, inexpensive, and reliable sensors have been made. It is also known that certain chemical species, even at low values can be toxic to humans [1]. Due to the volatile nature of ethanol, the most significant route of exposure is likely to be by inhalation. Ethanol manufacturing is continuous, enclosed processes with controlled occupational exposures. Potential exposures can occur during operations as sample collection, maintenance of equipment, and loading of trucks and/or rail cars. Occupational exposure limits in the USA and the main European countries are in the range 500-1000 ppm (1900 mg/m³), whereas in Germany the limit is 500 ppm. In the UK, Denmark, and the USA the occupational exposure limit is about 1900 mg/m3 1000 ppm. Volatile organic compounds (VOCs) in human breath had been identified as early as 1970 as a noninvasive indicator of health in an individual. Emissions from humans include hydrocarbons, alcohols, ketones, and aldehydes at ppb to ppm levels [2]. The breath of healthy individuals consists of about (13–1000 ppb) of ethanol gas [3].VOCs gas sensors based on non-biomaterial have been used extensively to detect the gases for their efficiency and broad applicability. However, the major problems associated with these gas sensors are their unsatisfactory selectivity and long-

term stability. In order to improve their properties, many efforts have been focused on the modification of semiconductor gas sensors by doping with elements or metal oxide. Apart from doping sensors, some coupling with metal oxide have also been reported to be promising as sensitive and selective gas sensors. The addition of a second component as a surface modifier is used both as active sites for redox processes and to promote free charge carriers to increase the electronic conductance of the oxide films [4].

As a requirement for a reliable bio-breath-analyzer fabrication that achieves all the sensor properties and able to overcome the problems as stated above including the costly materials used in conventional sensing methods and enhance the sensing properties. Blending is one of the useful methods to enhance the sensing properties. In this study roselle or Jamaica sorrel which was blended with chitosan gel has the same functional group as chitosan also, its chemical and physical properties give it a great possibility to be an attractive blending material to enhance chitosan sol-gel sensing properties. Roselle is planted for commercial purposes in west Africa, Malaysia and neighboring countries, as it is promoted by the departments of agriculture to be used in food and cosmetic industries [5], [6]. Recently Roselle was used as pH sensing material in an optical sensor due to the natural reddish color in roselle calyx [7].

Currently, the detection and sensing of ethanol gas is important for a variety of purposes including ethanol production, industrial chemical processing, fuel processing and use, societal applications, and physiological research on alcoholism [8]. Various kinds of gas detecting techniques are available in market most of them suffer from the high fabrication cost, limitation in sampling and analytical technical exist [9]. Lately, high sensitivity/selectivity sensors and analyzers are limited to the laboratory. Conventional techniques used to detect volatile organic compound gases such as metal oxide semiconductors have to deal with the problem of poor sensitivity at room temperature. Optical methods and carbon nanotubes techniques are also suffer from the disadvantages of high cost, need for trained personnel and difficulties in fabrication and achieving the sensor properties [10], [11]. Therefore, a developed and reliable gas analyzer is needed to monitor and detect the existence of ethanol gas in workplaces and measure the concentration of ethanol in human breath to prevent unwanted illness, and raise the awareness of alcohol consumers and help the authorities to monitor alcohol outlaw consumers.

The gas-analyzer sensor can be used in many applications such as the detection of toxic and combustible hazardous ethanol gas, the monitoring of emissions from chemical factories and other combustion processes, breathe analysis for medical diagnosis and quality control in the chemical, food and cosmetics industries.

2. RESEARCH METHOD

Conventional techniques of gas sensing used to focus on multi gases detection, which detect different kind of gases regardless of the gas concentration. The gas concentration should not be neglected as the gas concentration plays an important role in the gas analyzing technologies. Harianto et al, successfully designed neural network multi-detection system without varying the concentration of each gas [12]. Kim et al, designed a metal-oxide chemoresistive gas sensor to detect ethanol at different ppm values. Yang et al, investigated the sensing mechanism of ZnO based nanomaterials towards ethanol gas [10], [13]. However, both technologies suffer from the high operating temperature (200º to 500ºC). Hemmati et al, synthesized nanostructured SnO_2-ZnO as selective ethanol gas sensor materials to detect ethanol gas concentration as low as 100ppm [4].

Problems stated above, can be solved by improving the analyzer setup and the sensing properties of the sensing material. In order to improve the sensing properties, blending method was used in this work to blend chitosan with roselle extract, then depositing the blend on a golden substrate to produce a thin film sensing material. In current work a classified gas sensor setup was used to analyze the concentration of ethanol in human breath based on an improved sensing material. Moreover, this work aims to detect ethanol particle at lower ppm levels.

2.1. Chitosan-roselle Formation

Chitosan powder of particle grade synthesized from crab shells was supplied by Sigma–Aldrich and used as a sensing material. The particle grade chitosan powder with 99% purity was dissolved in mixture of distillated water and acetic acid 2% then stirred using a magnetic bar for 24 hours at room temperature to prepare the transparent chitosan smart gel. The solution was then filtered using a sintered glass crucible to remove any undissolved matter. To obtain a fresh roselle, flowers were cut and cleaned, and then their unwanted seeds were removed. The roselle flowers were washed then dried in oven at 40°C to remove water spots. They were next blended, then squeezed and filtered using a cheesecloth bag. To get the extract roselle a specific amount of methanol was added into the extract, and stirred using magnetic stirrer for 3 hours at speed of 400 rpm [14]. The final extracted roselle solution was blended with chitosan gel with a percentage

of 5% v/v. The blended chitosan-roselle solution was stirred using magnetic bar for 30 minutes to get homogenous chitosan-roselle blended solution. The electronic identification system was made by the following process which includes printed circuit board pattern, chitosan-roselle blend deposition finally, testing chamber design [15].

2.2. PCB Patterning and Deposition Process

For PCB patterning, golden PCB substrate was cut into sizes of 10mm by 20mm, followed by PCB washing using acetone and deionized water to clean the gold surface and remove any particles that may affect the conductivity and deposition process. The PCB was then cleaned again using acetone and dried.

The chitosan-roselle blend gel was coated onto the patterned gold surface using an electrochemical deposition technique as it shown in Figure 1. The technique was selected because it costs less compared to other techniques. Electrochemical deposition which is also known as the Sol-gel method, is conducted by depositing layers of thin film through chemical reactions such as hydrolysis and condensation [16]. Chitosan-roselle blend deposition onto the electrode is in response to the potential voltage it's a combination of two effects. First chitosan has a positive charge in acidic conditions, which will force it to assemble onto cathode electrode surface [17].

Secondly, chitosan is insoluble under basic form but water-soluble in acidic form. Therefore, hydrogen evolution reaction of the cathode surface increases, if the local pH increases. As a result, chitosan will become insoluble then deposited on the surface of the electrode.

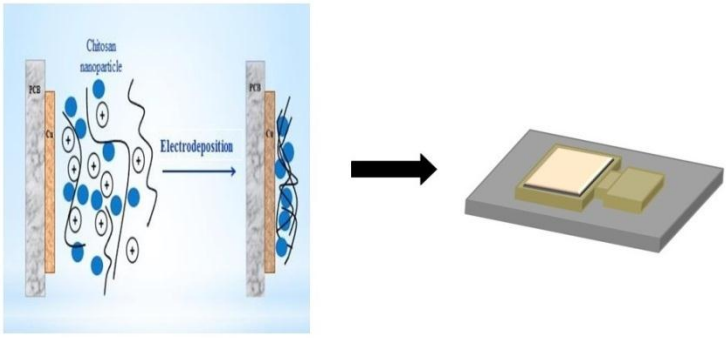

Figure 1. Electrochemical deposition process

2.3. Testing Chamber Design

A classified chamber was designed to handle the I-V testing as it shown in Figure 1. The proposed PCB was equipped with positive and negative contacts and placed in the chamber then connected to voltage resource. The supplied voltage was fixed at 3 volts. The output voltage was displayed as mV by high resolution voltammeter. Reading was recorded every 30 seconds, for five minutes continuously. Developed exposing technique was used to expose different concentrations of ethanol gas to the breath-analyzer sensor in order to determine the sensor performance and its properties such as sensitivity, recovery, repeatability and stability. The electrical testing of the breath-analyzer properties was in accordance to the experimental setup diagram as shown in Figure 2 [18].

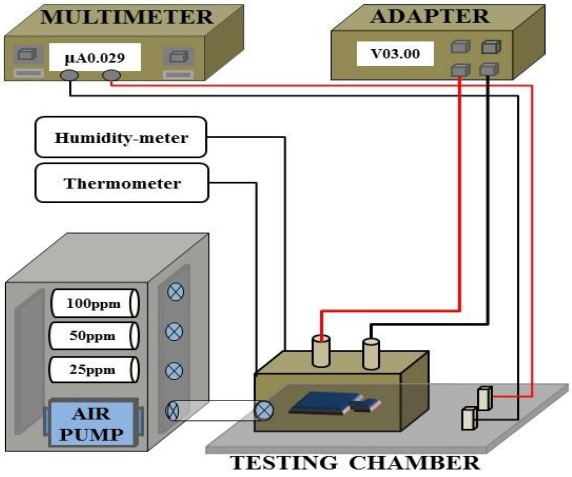

Figure 2. The breath-analyzer setup

3. RESULTS AND ANALYSIS

In this study, sol-gel deposition method was used since it offers a simplified fabrication process. Pattering was determined by the trace created by the electrode, using reliable fabrication techniques. The golden electrode was negatively biased to draw the chitosan (with a net positive charge due to the amine groups) out from the sol-gel. The current flowing through the electrolyte raised the pH at the cathode, allowing chitosan-roselle particles to be electrodeposited on the sensor surface. The chitosan-roselle particles were positively charged in acidic conditions, which allow them to assemble onto the golden surface, to form roselle-chitosan thin film [19]. To evaluate the sensing ability of the breath analyzer ethanol biosensor sensor, different concentrations of ethanol vapor were flowed inside the testing chamber as shown in Figure 2. The quantity of each concentration was controlled by regulating valves. Then, the breath-analyzer sensor was placed inside the testing chamber which connected to thermometer and humidity-meter to detect the temperature and humid changes inside the chamber during the I-V testing.

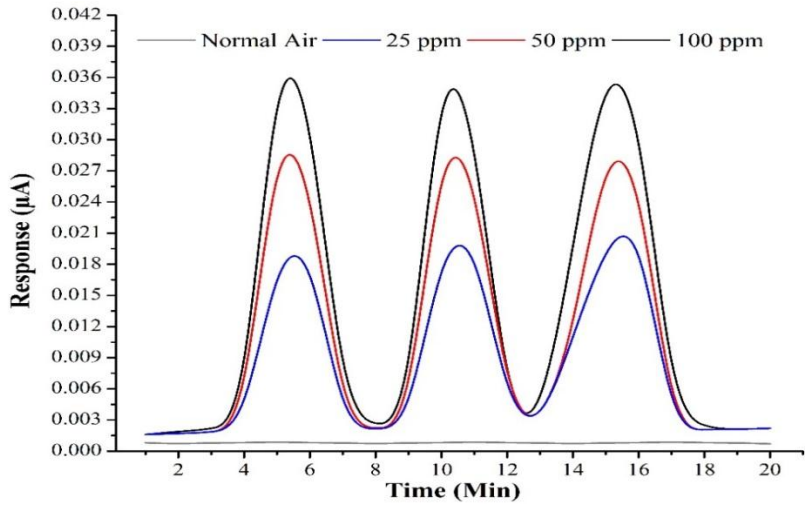

Figure 3. The response of the breath-analyzer to normal air and different concentrations of ethanol gas

Figure 3, shows the response of the breath-analyzer sensor exposed to normal air and different concentration of ethanol vapor. The variations of ethanol vapor were 100ppm, 50ppm and 25ppm. As can be clearly seen the breath-analyzer exhibited very small response when its surface was exposed to normal air where, the average response values for three times measurements were within the range of 0.0011 µA to 0.0013 µA. From the plotted graph, the breath-analyzer showed a higher Micro-ampere peaks response in the

presence of higher concentration of ethanol vapor while lower peaks were observed when the analyzer was exposed to a lower ppm of ethanol vapor.

The breath-analyzer was highly sensitive to ethanol gas at 100ppm concentration with 0.036 µA response value, while at 50ppm and 25ppm the outcome responses were about 0.027 and 0.018 µA, respectively.

Then, once the vapor of ethanol gas was evacuated from the chamber, the electrical response values for all different concentrations conditions decreased to the original value in 4 min, as shown by the drop in the plotted graph. This implies that the breath-analyzer ethanol biosensor produced in this work showed a good response, and exhibit a fast recovery. The response time of the breath-analyzer is defined as the initial time that required by the sensor to sense the presence of the target molecules on its surface, which was approximately less than five minutes for each concentration.

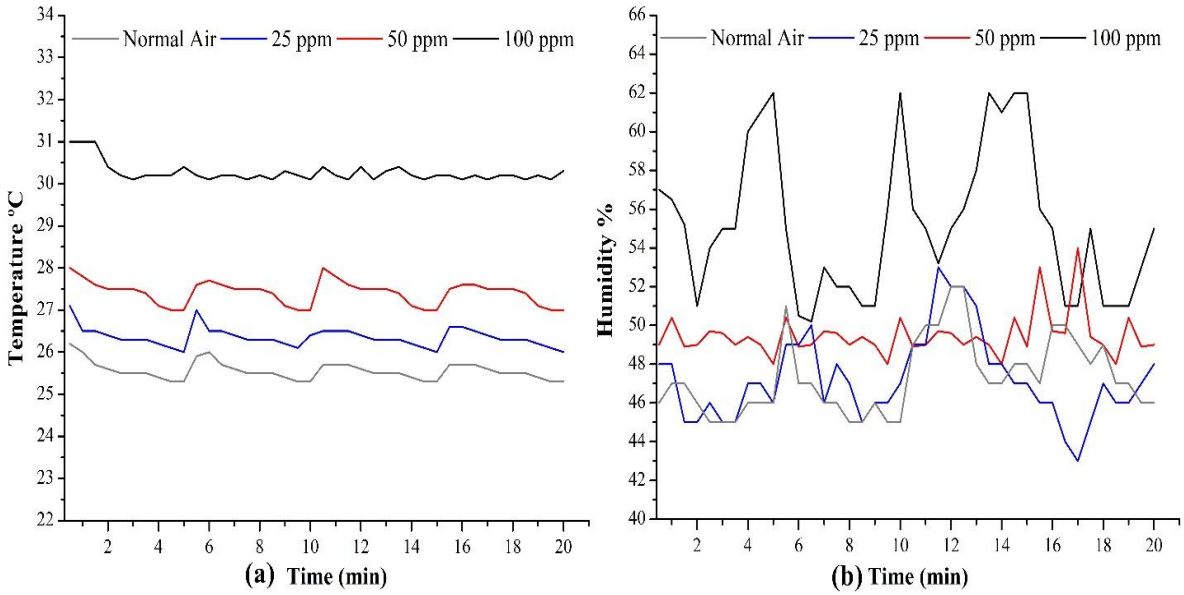

Figure 4. The change of temperature (a) and the change of humidity (b) inside the testing chamber

Moreover, the plotted graph illustrates that the breath-analyzer showed good repeatability and stability as the measurements were taken. Stability was indicated by the ceaseless increase in response without a significant signal fluctuation in the graph. Figure 4(a) and (b), confirms the stability of the analyzer when the measurements were taken, where the internal temperature was in range of 26Cº to 31Cº while the humidity percentage inside the testing chamber was between 45% to 60%. Although the measurements were repeated three times uninterruptedly, the alcohol breath-analyzer showed almost the same response values for each exposing time which was 5 minutes for each peak.

FTIR analysis was carried out to investigate the interaction between pure chitosan and chitosan-roselle blend as shown in Figure. 6, as the characteristic of N-H and OH groups in chitosan-roselle blend are the main component in the thin film structure to sense the ethanol gas particles.

In the spectra of the pure chitosan deformation peak appeared at 3242.10cm^{-1} . The bands at 2921.66 and 2166.82cm^{-1} are assigned to C-H stretching. Two functional group peaks were observed in the spectrum of pure chitosan which were the C=O stretching vibration of -NHCO- and the N-H bending vibration of -NH_2 appearing at 1634.81cm^{-1} and 1542.16cm^{-1} [20].

The FTIR spectrum of the chitosan-roselle blend displays a very board band at 3749.02cm^{-1} corresponding to the stretching vibration of amine and hydroxyl groups, while band at 3235.06cm^{-1} is related to the O-H vibration. The band at 2924.10cm^{-1} is assigned to the CH_2 asymmetric stretching. Bands at 2162.44 and 2031.63cm^{-1} are related to C≡C stretching. A carboxylic acid functional group C=O stretching is appeared at 1775.45cm^{-1}. Bands at 1380.14 and 1229.58cm^{-1} are attributed to the C-H and C-O stretching

respectively, and those at 1152.33, 1062.59 and 1023.73cm^{-1} are indicative of the C-O stretching vibrations, while at 897.51cm^{-1} is assigned to C-H stretching.

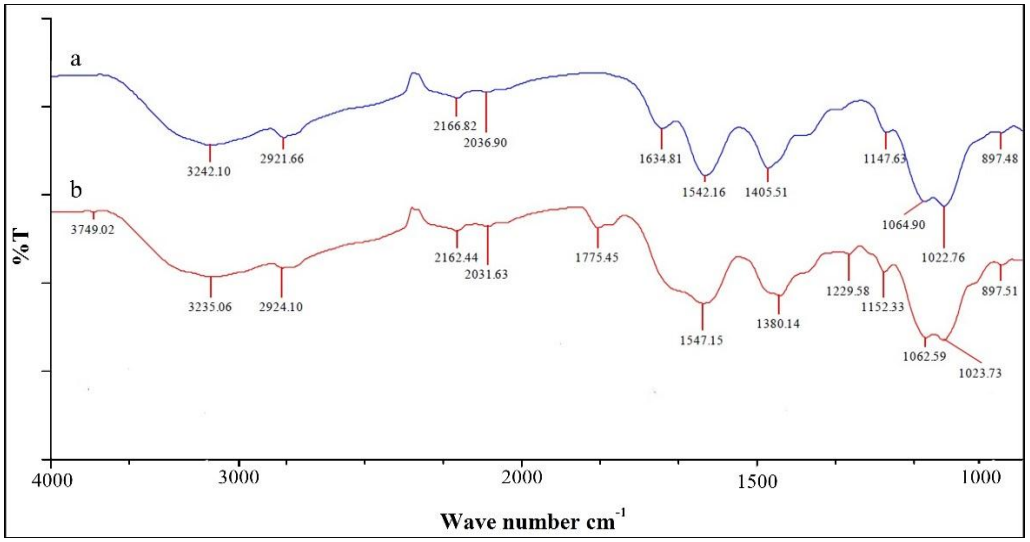

Figure 6. The FTIR spectra of pure chitosan (a) and chitosan- roselle blend (b)

4. CONCLUSION

This study has shown the effectiveness of using the chitosan-roselle blend to enhance the sensing of the Alcohol breath-analyzer biosensor through sol-gel deposition method. The breath-analyzer exhibited high sensitivity and selectivity towards ethanol gas with low detection limit which can detect as low as 25ppm of ethanol particles. It is capable to determine the concentration value of ethanol gas which can be featured and used in alcohol breath testing devices. The deposited roselle-chitosan the film on the golden surface PCB has shown better properties, good response time, and excellent recovery and repeatability properties, which are indeed promising to improvise the sensitivity of alcohol breath-analyzer. Those results were validated by FTIR spectra which shown that the chemical interaction between chitosan and roselle extract which made a homogenous chitosan-roselle sensing material blend.

REFERENCES

[1] Eljali AMS, Nainggolan I, Hashim S, "Nasution TI. Highly Response and Sensitive Copper Sensors Based on Chitosan Films", *Adv Mater Res*, 2015; 1125: 255–259.
[2] Health Council of the Netherlands, "Ethanol (ethyl alcohol); Evaluation of the Health Effects from Occupational Exposure", The Hague: Health Council of the Netherlands, 2006.
[3] Fenske JD, Paulson SE, "Human Breath Emissions of VOCs", J Air Waste Manage Assoc. 1999; 49: 594–598.
[4] Hemmati S, Anaraki Firooz A, Khodadadi AA, Mortazavi Y, "Nanostructured SnO2–ZnO sensors: Highly sensitive and selective to ethanol", Sensors Actuators B CheM, 2011; 160: 1298-1303.
[5] Eslaminejad T, Zakaria M, "Morphological Characteristics and Pathogenicity of Fungi Associated with Roselle (Hibiscus Sabdariffa) Diseases in Penang, Malaysia", *Microb Patho*, 2011; 51: 325–337.
[6] Hopkins AL, Lamm MG, Funk JL, Ritenbaugh C, Hibiscus Sabdariffa L, "In the Treatment of Hypertension and Hyperlipidemia: A Comprehensive Review of Animal and Human Studies", *Fitoterapia*, 2013; 85: 84–94.
[7] Karim NHA, Ahmad M, Herman MO, Mokhtar AM, "Optical Sensing Material for pH Detection based on the Use of Roselle Extract", *Sains Malaysiana*, 2008; 37 :59–63.
[8] Zhang D, "Multi-walled Carbon Nanotube Film Sensor for Ethanol Gas Detection", *TELKOMNIKA Indones J Electr Eng.* 2013; 11: 6120–6126.
[9] Srivastava AK, "Detection of Volatile Organic Compounds (VOCs) using SnO2 Gas-Sensor Array and Artificial Neural Network", *Sensors Actuators, B Chem*, 2003; 96: 24–37.
[10] Kim ID, Rothschild A, Tuller HL, "Advances and New Directions in Gas-Sensing Devices", *Acta Mater*, 2013; 61: 974–1000.
[11] Jiang Z, Wang J, Meng L, Huang Y, Liu L, "A Highly Efficient Chemical Sensor Material for Ethanol: Al2O3/Graphene Nanocomposites Fabricated from Graphene Oxide", *Chem Commun (Camb)*, 2011; 47: 6350–6352.
[12] Rivai M, Purwanto D, "Implementation of Electronic Nose in Omni-directional Robot", *Int J Electr Comput Eng.*

2013; 3: 399–406.
[13] Yang Z, Huang Y, Chen G, Guo Z, Cheng S, Huang S, "Ethanol Gas Sensor based on Al-doped ZnO Nanomaterial with many Gas Diffusing Channels", *Sensors Actuators, B Chem*, 2009; 140: 549–556.
[14] Yurdiansyah A, Suhartanti D, "*Test Activities Antifungal Methanol Extract Red Flowers Rosella Calyx (Hibiscus sabdariffa L .) on Candida albicans , As In Vitro , and Screening Phytochemicals"*, Proceeding of the International Conference on Green World in Business and Technology (IC-GWBT2012). 2012; 116–122.
[15] Aphirakchatsakun W, Angkanaporn K, Kijparkorn S, "The Effect of Roselle (Hibicus sabdariffa Linn.) calyx as Antioxidant and Acidifier on Growth Performance in Postweaning Pigs", *Asian-Australasian J Anim Sci*, 2008; 21: 574–581.
[16] Kiani MJ, Samadi J, Yaghoubyan SH, "High Sensitivity Of Tin Oxide Sensor by Sol-Gel Method", *Int J Nano Devices, Sensors Syst*, 2012; 1: 46–52.
[17] Henini M, "Handbook of Thin-Film Deposition Processes and Techniques", vol. 31. 2000.
[18] Nasution TI, Nainggolan I, Hutagalung SD, Ahmad KR, Ahmad ZA, "The Sensing Mechanism and Detection of low Concentration Acetone using Chitosan-based Sensors, *Sensors Actuators, B Chem*, 2013; 177: 522–528.
[19] Martínez-Huitle CA, Jara CC, Cerro-Lopez M, Quiroz MA, "Chitosan-Modified Glassy Carbon Electrodes: Electrochemical Behaviour as a Function of the Preparation Method and Ph", *Can J Anal Sci Spectrosc*. 2009; 54: 53–62.
[20] Roshida M, Irwana N, Tuluz Ikhsan N, Khairel Rafezi A, Nazree D, "Roselle Blend Film Sensor (RBFS) for Detecting Fertilizer Concentration of Grape Tree", *Appl Mech Mater.* 2015; 754–755: 606–611.