

# Highly Response and Sensitivity Chitosan-Polyvinyl alcohol Based Hexanal Sensors

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**Abstract.** This work is to study the sensing properties of chitosan-polyvinyl alcohol film sensors upon hexanal gas exposure using vapour sensing technique. The sensor fabrication process was done using electrochemical deposition method by deposit the sensing materials on the gold patterned electrode with chitosan/PVA. The response value of chitosan-PVA film sensors towards hexanal was taken as an output voltage using electrical testing method. In this study, 1.75% of chitosan with 5% of PVA were mixed with the ratio of (95:5) was tested upon exposure to hexanal gas. The concentration of the hexanal was varied as 10 ppm, 20 ppm, 30 ppm. It was found that the chitosan-PVA film sensors showed fast response, stable, good stability, good recovery, repeatable and good sensitivity towards hexanal exposure. The morphology of the pure chitosan and chitosan-PVA was analyzed by scanning electron microscope (SEM) and the interaction between chitosan and PVA was examined by Fourier Transform Infrared Spectroscopy (FTIR). The FTIR results indicate the changes in characteristics of the spectral peaks due to the formation of the intermolecular bonds between chitosan and PVA. The SEM morphology of the composites showed flat smooth surface that be a sign of uniform distribution of chitosan and PVA mixture throughout the films.

## 1 Introduction

Food deterioration that occurred effect the quality and decrease the shelf life of the food itself. This is caused by the lipid oxidation that occurred during food storage. This process results in alteration of flavour, texture and nutrition value in the food [1]. In addition, the autooxidation in wood pellets will released hexanal as a major emitted gas during storage [2]. Besides that, a study reported that they develop hexanal as an odour reference standard for sensory analysis of drinking water. The off flavour in drinking water will reduce intake drinking water among peoples and less of confidence in the water utilities. The off-flavour may be caused by contaminants in water sources, corrosion of metal pipes and new plumbing materials. Hexanal was chosen as good candidates for odor reference standard because it was stable during the sampling process and reproducible results [3]. Hexanal also

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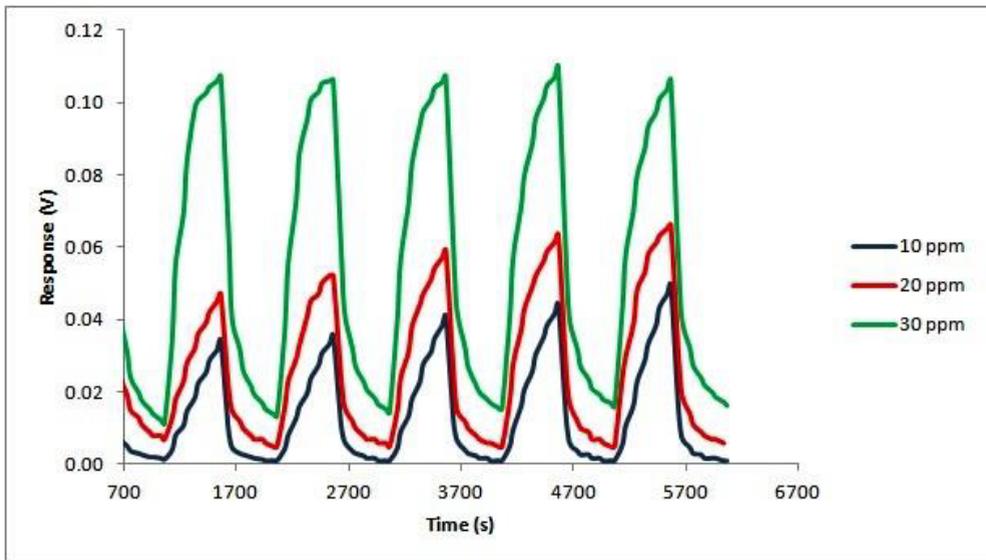
used as food additive and it was detected in lung cancer blood [4,5]. So, it is important to have a device to detect hexanal gas in order to be applied in any fields that required to monitor the concentration level of hexanal. Current equipment to detect the concentration of hexanal was gas chromatography (GC) that has drawbacks such as expensive, large space used, required specialist to operate the equipment and high in maintenance utilities. Thus, a device with low cost, easy to operate and user friendly needed to overcome the drawbacks of GC. On the other hand, shrimps, lobster, crabs or krills were exoskeleton creatures that have chitin, one of the most plentiful renewable organic resources in nature. Derivation of chitin will produce polyaminosaccharide compound that also known as chitosan [6]. Chitosan was second most abundant polymer in nature after cellulose. Chitosan is a polysaccharide composed of B-(1,4)-linked D-glucosamine residues (deacetylated unit) with a variable number of randomly located N-acetyl-glucosamine groups (acetylated unit) [7]. It consist of two types of reactive functional groups amino (NH<sub>2</sub>) at C-2 and hydroxyl (OH) at C-3 and C-6 position on the backbone along with interdispersed acetamido groups [8]. Chitosan has excellent characteristics including good chemical inertness, high mechanical strength, biodegradability, biocompatibility, high-quality film forming properties, and low cost [9]. Polyvinyl alcohol (PVA) is a non-toxic, water soluble polymer having a strong film forming ability with very high dielectric strength, good charge storage capability, high mechanical tensile strength and dopant dependent electrical and optical properties [10]. PVA is an inexpensive hydrophilic semi-crystalline polymer. This polymer has excellent film forming properties and can produce effective electrolytes after doping with potassium hydroxide (KOH) solution [11]. During to the good properties of PVA, it was believed that it has ability to influence the sensing performance of chitosan film sensor. In this study, we investigated the capability of Chitosan-PVA compared to pure Chitosan as sensing materials upon different of concentration hexanal. The electrical testing was done in order to check the performance of the sensor which including response, stability, sensitivity, repeatability and recovery.

## **2 Experimental**

Chitosan solution was prepared by dissolving 1.75 g of chitosan powder (low molecular weight, Sigma Aldrich) in 100 ml of 2% aqueous Acetic Acid (99.9% purity, HmBG). The mixture was stirred continuously at room temperature for 24 hours. Polyvinyl alcohol (Average MW = 200000, Sigma Aldrich) was dissolved in water and stirred for 1 hour at temperature 80°C. The PVA solution was added dropwise in the chitosan solution that prepared from previous procedures. The mixture was stirred continuously at room temperature for 1 hour. Chitosan-PVA solution will form into film by electrochemical deposition process by a piece of patterned electrode was dipped into chitosan/PVA solution and was subjected to required deposition voltage and deposition time. The deposited chitosan-PVA film were hard baked on vacuum oven with temperature of 100°C to remove excess water that existed on the film. Then, the sample was cooled at room temperature. The electrical testing was tested in order to check the performance of the sensor which including stability, sensitivity, output voltage, repeatability and recovery. The chitosan-PVA film sensor was placed in a chamber and connected with power supply and the output was recorded by Digital multimeter (Model : Sanwa CD771). The sensor was exposed to hexanal and dry air alternately. The output voltage was recorded for every 30 seconds for 5 minutes to hexanal vapor and 5 minutes to dry air to complete one cycle.

### 3 Results and Discussion

Fig. 1 shows graph response of CS-PVA film sensor towards hexanal exposure. The response of the sensors during hexanal exposure was taken as an output voltage. As recorded, the response value of CS-PVA increased when exposed to the hexanal. The response of CS-PVA film sensor increased fastly within 5 minutes for 10 ppm, 20, ppm and 30 ppm respectively. CS-PVA film sensors gave good response during 5 cycles of measurement when exposed to hexanal vapour. In addition, the Chitosan-PVA composite film sensors yielded repeatable readings at when hexanal vapour was exposed within 5 cycles. The recovery of CS-PVA film sensor was satisfactory since the output response recovered gradually when hexanal was replaced by dry air. Fig. 2 shows the root mean square (R2) of CS-PVA was fit to regression line which is 0.9979. This indicates that the response of CS/PVA towards each hexanal concentration was around the average value. Fig 3 and Fig 4 shows the operating temperature ( $^{\circ}\text{C}$ ) and humidity (%) values that were taken during the measurement of the CS-PVA film sensor at room temperature. The range of the operating temperature was between  $26^{\circ}\text{C}$ - $33^{\circ}\text{C}$  during the measurement was collected. This indicates that CS/PVA film sensors able to operate at room temperature without any fluctuation readings.



**Fig. 1.** Response (V) of Chitosan/PVA Sensor towards Hexanal.

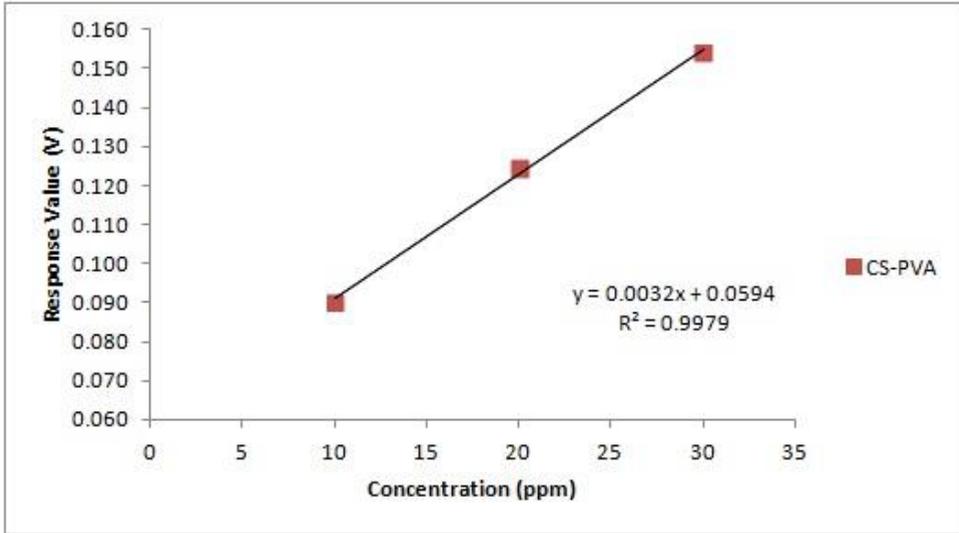


Fig. 2. Maximum Response of CS/PVA against concentration of Hexanal (ppm).

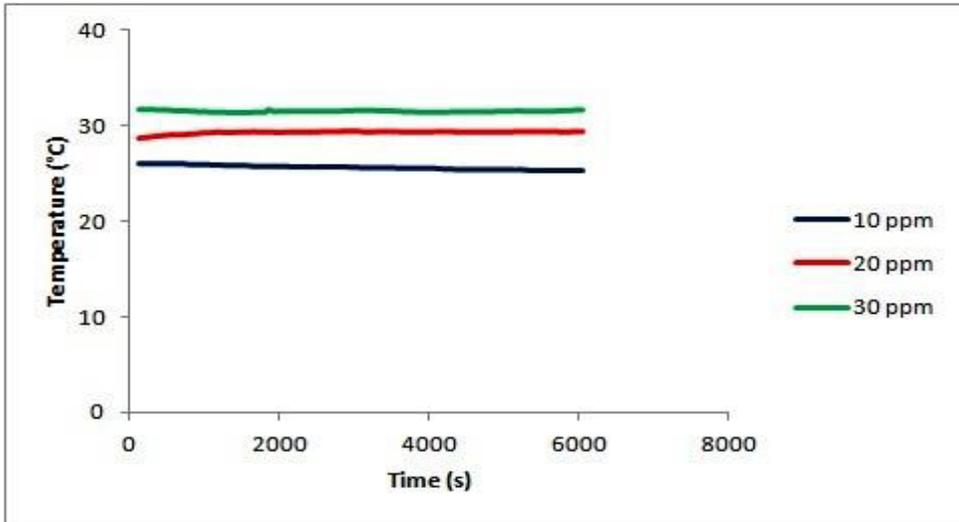


Fig. 3. Operating Temperature (°C) of CS/PVA against concentration of Hexanal.

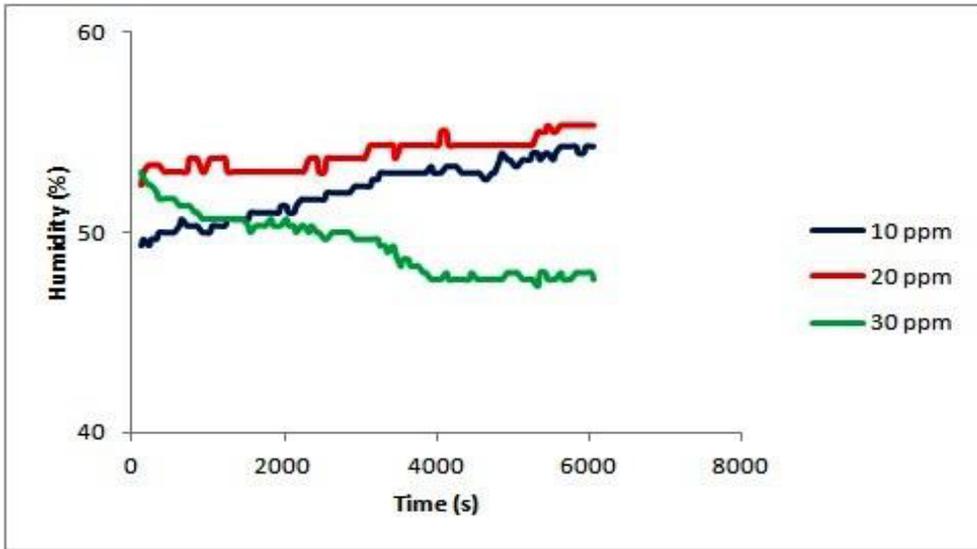


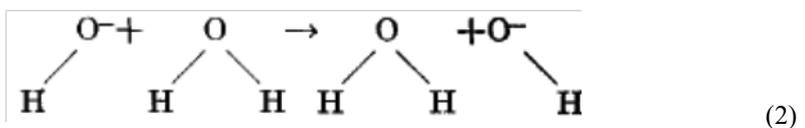
Fig. 4. Humidity (%)of CS/PVA against concentration of Hexanal.

### 4 Sensing Mechanism

The sensing mechanisms of the polymer sensor films occurred when the composite polymer is exposed to water vapour. The water vapor will be chemically adsorbed (chemisorption) at the activated sites of the polymer composites. The water molecules will be dissociated at the vapor stage as shown in Eq. 1.



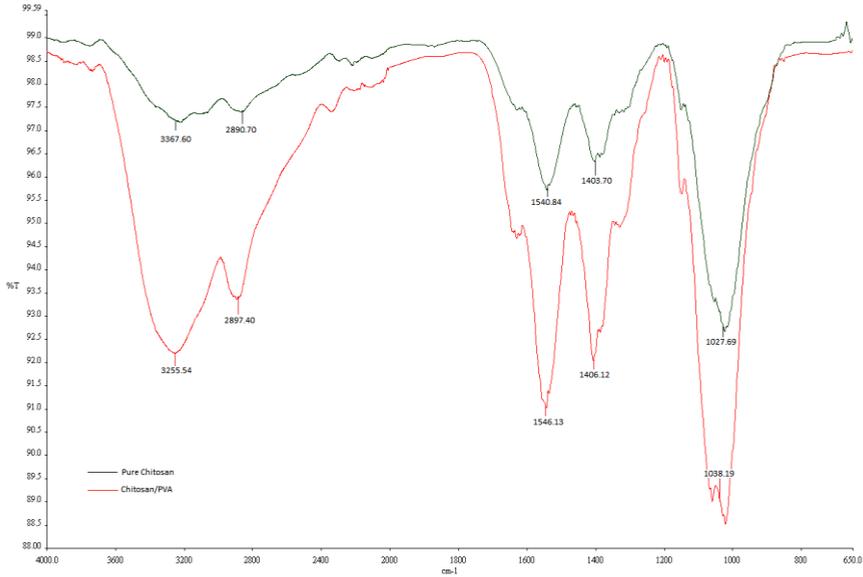
The hydroxyl group (as shown in Eq. 2) of each water molecule will be adsorbed at the chitosan cations and providing mobile protons. This interaction will form a layer surrounding the chitosan cations. The subsequent water vapor will form a second layer on the first layer. This process will form a number of stack layers. This will lead the vapor molecules have more mobile protons resulting the increasing in the conductivity values as well as increase the output voltage during the electrical testing [12]. During recovery process, oxygen molecules will be chemisorbed onto the surface of the chitosan particles when the sensor is exposed to normal air. Under certain input voltage, the amount of free electrons moving randomly in the conduction band is reduced as the chemisorbed oxygen traps them and transfers them from one particle to another. This results in an increase in resistance and a decrease in output voltage of the chitosan film until the oxygen species are saturated [13].



When hexanal gas vapour is exposed on the surface of the CS-PVA film sensor, the gas molecules of hexanal will make a contact with chemisorbed oxygen on the film sensor surface as shown in Eq. 3. This will make the electrons release freely within the CS-PVA surface. The equation involved as follows:

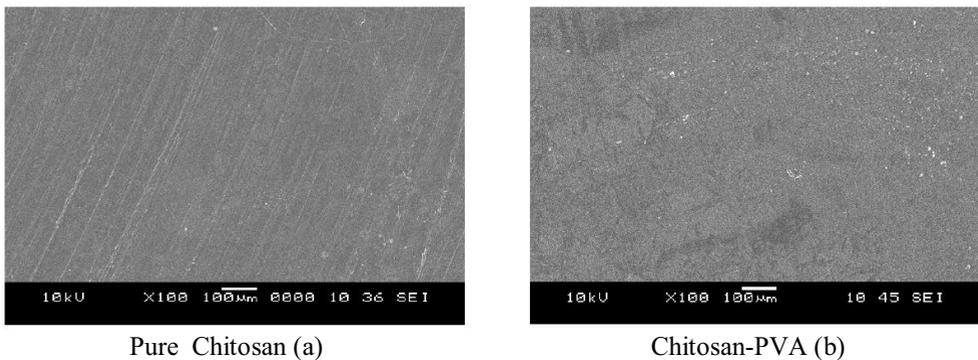


The contact reaction between the analyte gas and sensor surface will release electrons and water molecules. These free electrons that occurred in conduction band will influence the increment of the response of the sensor [2].



**Fig. 5.** FTIR Spectra of Chitosan Film and Chitosan-PVA Film.

Pure Chitosan films showed peak at 3367.60 cm<sup>-1</sup> that indicated for the –OH and NH<sub>2</sub> stretching. Measurement spectra of 2890.70 cm<sup>-1</sup> for –CH stretching, 1027 cm<sup>-1</sup> was noted for C–O–C stretching, 1540.84 cm<sup>-1</sup> for –NH bending of NH<sub>2</sub> (amide II) and 1403.70 cm<sup>-1</sup> for –CH wagging coupled with –OH groups of chitosan. The addition of PVA in the chitosan caused a decrease in the intensity of the band at 1540.84 cm<sup>-1</sup> of chitosan. CS-PVA composite exhibits an absorption band around 3255.54 cm<sup>-1</sup> and 2897.40 cm<sup>-1</sup> due to the –OH stretching and –CH<sub>2</sub> asymmetric stretching from PVA [14].



**Fig. 6.** SEM image of pure chitosan film (a) and chitosan-PVA film (b).

Based on the surface morphology obtained from SEM, chitosan film shows a smooth surface with some straps existed as depicted in Fig. 6. Meanwhile, the surface of the

composite film made of chitosan and PVA is more homogenous and flat surfaces that indicates the uniform distribution of chitosan and PVA in the films. This uniformity characteristics may caused by the interaction of functional groups of  $-NH_2$  in chitosan and  $-OH$  in PVA [15].

## 5 Summary

Chitosan-PVA film was found as a good sensing material to sense various concentration of hexanal. chitosan-PVA film sensors showed good sensing properties which include good response, stability, sensitivity, repeatability and recovery properties toward hexanal vapor exposure. The low cost production and ease of fabrication process make chitosan-PVA sensors become advantageous to be applied in various fields.

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