

HIGHLY SENSITIVE SAFROLE SENSOR BASED ON CHITOSAN MODIFIED ELECTROSPUN POLYACRYLONITRILE NANOFIBERS

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ABSTRACT

Safrole is one of the main precursors in the production of an amphetamine-type stimulant (ATS) drugs, N-methyl-3,4-methylene-dioxyamphetamine (MDMA or ecstasy). In the practical application, safrole should be able to be detected rapidly and accurately. This paper aims to report the main characteristics of quartz crystal microbalance (QCM coated with polyacrylonitrile (PAN) nanofibers to detect safrole. Here, the fibers were prepared using electrospinning and deposited directly on the both Au surfaces of the QCM followed by drop coating with chitosan solution. For comparison, we also characterized the QCM coated with PAN nanofibers only and the QCM coated with drop cast chitosan only. As results, the sensors without combination of PAN nanofibers and chitosan exhibited very low sensitivity, while that of combination presented an excellent response to detecting safrole vapor at ambient temperature. In more detail, the sensor with combination of PAN nanofibers and chitosan possess excellent sensitivity of 0.119 Hz/ppm, good reversibility, fast response (40 s), with relatively stable and selective for safrole detection. Hence, such promising QCM

sensors based on chitosan modified electrospun polyacrylonitrile nanofibers could not only potentially allow for detecting safrole, but also flexibility in designing and developing novel QCM sensing systems for other drugs and narcotics.

Keywords : Quartz Crystal Microbalance; Safrole; Ecstasy; Precursor, Nanofiber polyacrylonitrile

INTRODUCTION

In recent year, the drug abuses have been growing rapidly and reaching various levels of ages. The smuggling of those illicit drugs has spread worldwide. Since 2010, the quantity of drugs seized globally has averaged around 4-5 tons ([United Nation, 2017](#)) and rapidly growing until present days. Detecting and counteracting the illegal trade remains a problem faced by law enforcement worldwide. The efforts to find the most effective and efficient way of identifying narcotics and its raw materials (precursors) is remain needed. One of the precursor types used to produce amphetamine-type stimulus (ecstasy) is safrole. Safrole is the main ingredient of producing the drugs N-methyl-3,4-methylenedioxyamphetamine (MDMA), and belongs to the category of narcotic precursor group 1. It is used as a precursor for the manufacture of narcotic substances type 3,4-methylenedioxy metham-phetamine (MDMA) or known as ecstasy ([D. Barceloux, 2012](#)).

There are many classic analysis methods applied for detecting drugs, including the use of a chromatographic technique such as liquid chromatography (LC) and gas chromatography (GC) coupled to mass spectrometry (MS) analyzers ([K. Honeychurch, 2016](#)), ([K. Saito, et al, 2011](#)) . While the used of chromatographic technique and coupled with mass spectroscopy analyzers offers highly sensitive and accurate detection, that technique also has a disadvantage such as they are not the portable, not easy to operate and costly instrument. Moreover, the necessity of a mobile, easy to use

and cheap analytical instrument for drugs detecting is very desirable to replace those classic analytical techniques.

In recent years the development of a gas sensor to detect the presence of specific gas in the air is rapidly growing. A lot of gas sensor has been developed based on their sensing mechanism including photoelectric sensors (L. Aba, et al 2014), resistance sensor (S. N. Hidayat, et al, 2016), optical sensor (M. Evyapan, et al, 2016), amperometric sensor (X. Wang, et al, 2014) and acoustic wave sensor (N.wang, et al, 2014) with different material structures. Quartz crystal microbalance (QCM) is one example of acoustic wave (AW) sensor platform based on acoustic-electric effect and mass deposition. A QCM sensor offers an accurate, real-time detection, and convenient sensors with high sensitivity response that is widely used as gas sensors and also as humidity sensors (S.N. Hidayat, et al, 2017). Amongst others, nanostructured materials have become one of the most likely used as active layer in the sensor devices especially in gas sensing devices (Y.F.Sun, et al, 2012). The nanostructured material especially nanofiber materials have an advantage when used as active layer in sensor devices including the large specific surface area, high porosity and interconnected porous structures that the nanofiber possessed (Chotimah, et al 2016). Various studies have been done investigating the improved sensitivity of gas sensor that used nanostructured materials compared to other casting methods (Y.Jia, et al, 2017). The literature indicated that the increased sensitivity is due to the increase of the specific surface area of the nanofibers (Y.Jia, et al, 2014).

In this study, we aim to develop a safrole gas sensor based on QCM technique used polyacrylonitrile (PAN) nanofibrous materials modified by chitosan as an active sensing layer. We used PAN nanofiber because it is one of the common materials used in the nanofiber fabrication. PAN nanofiber also offers high mechanical stability, insoluble water, and hydrophobic properties. The hydrophobic properties become an essential issue in the development of gas sensor based on QCM technique due to its the high relative humidity

dependence. The used of the hydrophobic materials in QCM based gas sensor can decrease the relative humidity in the QCM sensors.

EXPERIMENTAL

Material

Polyacrylonitrile (PAN) polymer with a molecular weight of 150,000 from Sigma-Aldrich was used for the preparation of the nanofiber. Chitosan with medium molecular weight from Sigma-Aldrich used to modify the PAN nanofiber. Non-ionic surfactant Triton X-100 was purchased from Merck, Germany. The solvents N, N-dimethyl formamide (DMF), and acetic acid 99% was purchased from Merck, Germany. Commercial safrole precursor with 96% purity used as main analytes. Other analytes for selectivity sensing including ethanol, acetone, benzene, toluene, and xylene were purchased from Merck, Germany. The AT-Cut QCM sensor with the gold electrode and 10 MHz resonant frequency were purchased from OpenQCM, Novaetech, Italy. All above materials used as received without any further purification.

Preparation of Polymer Solution

The PAN solution was prepared with a concentration of 6% by using 5.0 ml DMF solvent. The PAN mass of 0.371-gram inserts 5.0 ml of DMF solvent into 10 ml beaker then stirrer for 60 minutes at temperature of 60 °C. After one hour of stirring, the non-ionic surfactant Triton X-100 (1%) was added to the PAN solution and stirring for another 30 minutes until homogeneous solution was achieved. The 0.01 % chitosan solution was produced by dissolving the 0.01 % chitosan in 2% acetic acid aqueous solution and stirred for 60 min at ambient temperatures.

Fabrication PAN Nanofiber Modified Chitosan

The set-up for deposition of nanostructured membranes on the electrode of QCM is depicted in Fig.1. The polymer solution of PAN was put into a 10 mL

syringe, with a pin-pointed end ($d = 0.5$ mm), given a voltage of 10 kV with a distance of 15 cm to the collector then placed as shown in Fig.1. Electrospinning is performed for 60 seconds, on each side of the QCM electrode. Fiber shooting was performed alternately on both sides of each QCM electrode for 30 seconds. After the PAN nanofiber dried, 10 μ L of the 0.01 % chitosan solution was then drops casting on PAN nanofiber membrane using Micropipette (Capp C100-1 series JB11239) for both sided QCM. The PAN nanofiber modified chitosan then dried until residual solvent fully evaporated.

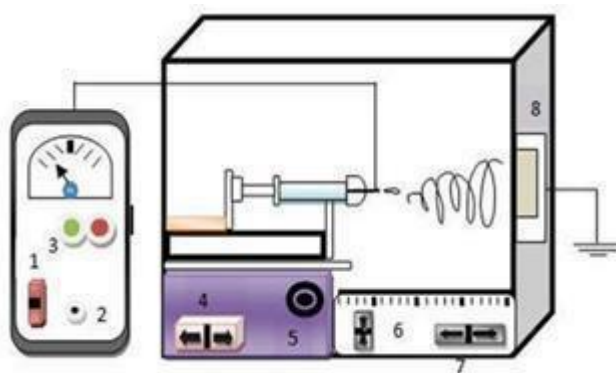


Figure1. Experimental set-up of electrospinning

Measurement of Sensing Properties

PAN-chitosan sensor in conducting sensing experiment using the static method with closed chamber size (1.2 L) at ambient temperature. The concentration of analytes injected into the chamber is calculated partially per million (ppm) according to the following equation:

$$C = \frac{22,4 \rho TV}{273 MV} \times 10^3 \quad (1)$$

where C is the concentration of safrole (ppm), ρ is the density of liquid safrole (g/mL), T is the testing temperature (Kelvin), Vs the volume of safrole (μ l), M is the molecular weight of safrole (g/mol), and V is the volume of the chamber (L). The sensing properties of the sensors were examined by measuring the resonance frequency shifts of QCM resulting from the additional mass loading.

The resonance frequencies were measured by the frequency counter, and the data from the sensors were recorded by a personal computer (J.Wang, et al, 2012), (N.Wang, 2012).

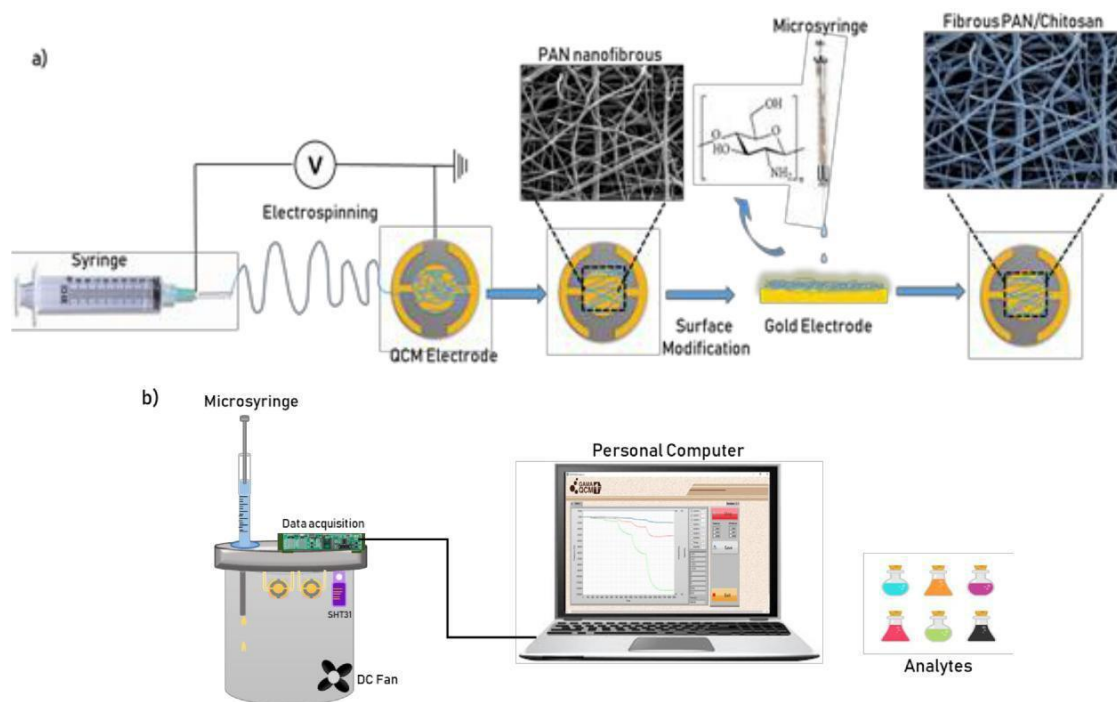


Figure 2. a) Schematic fabrication of sensing membranes on QCM, b) and the safole sensing system.

RESULT AND DISCUSSION

The safole sensing properties of Chitosan structured polyacrylonitrile fibers on QCM were investigated by measuring the frequency shifts when the fibrous membranes were exposed to safole vapors. During the process of exposure, the sensor responses for each safole concentration were obtained from frequency shift between the corresponding frequencies at the beginning and the end of the exposure process. Fig. 3 presents the frequency response of PAN-chitosan sensor with various coating loads sequential exposure as a function of safole concentration (100, 200, 500, 1000 and 2000 ppm) in the temperature-controlled measurement chamber. The blank sensor shows small response to exposure to 100 ppm to safole. The frequency shift of the blank QCM sensor for

concentration variations of 100, 200, 500, 1000 and 2000 ppm of safrole vapor were 0.05, 0.65, 2.25, 4.95 and 9.40 Hz, respectively. It appears that the amplitude response of the sensor increases gradually by increasing the concentration of safrole.

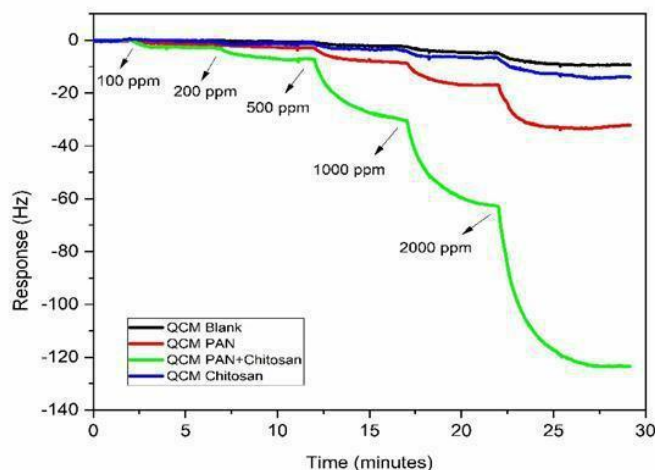


Figure 3. Sensor response for exposure to safrole vapor

PAN nanostructured sensors have large specific surface areas, high porosity, and interrelated porous structures. The response obtained for PAN sensor is better than the other two sensors are a blank sensor and chitosan sensor. Specifications contained electrode surface area nanofiber make interaction safrole vapor exposure becomes greater. The response results in PAN sensor are 1.50, 3.05, 8.60, 16.95, and 33.3 Hz, respectively. The results for chitosan sensor is smaller than the sensor PAN results. This occurs due to coatings made by using drop casting method or solution droplets over QCM electrodes. The less stable response was achieved with chitosan sensor when exposure to the safrole vapor.

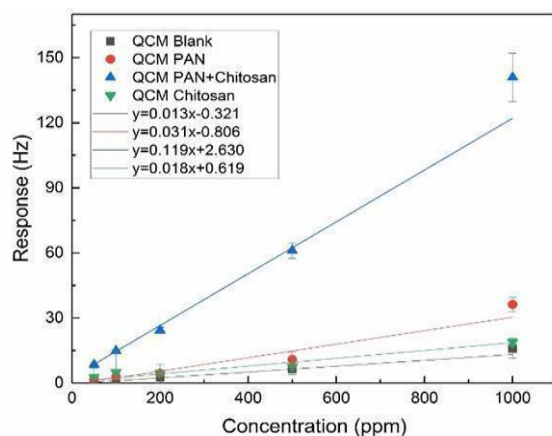


Figure 4. Frequency shift (response) versus safrole vapor concentration for obtaining the sensitivity of each sensor.

Figure 4 shows the sensitivity of PAN-based QCM sensors with chitosan coatings in detecting safrole vapors with concentrations of 50-1000 ppm. Based on the safrole sensing properties of PAN-chitosan sensors, we conclude two advantages of this PAN-Chitosan sensor. For One side, the unique structure and high porous configuration of the PAN membrane are useful for achieving a rapid response as well as through the rapid spread of the analytical vapor. The PAN-chitosan membrane layer can provide an enhanced diffusion path for safrole molecules. Increased vapor and mass diffusion in transport in the course of sensing. In addition, the magnitude of the PAN-chitosan membrane type also facilitates most of the oscillation switching to produce a faster response.

For this result, an analysis of the frequency shift of the QCM sensor is in a stable state when exposed by the analyte as well as the linear relationship between the variables. The purpose of this analysis is to see the QCM sensor stability capability when exposed to analyte continuously for twenty days. Fig. 5(a) shows the response of the sensor to a certain concentration taken for five days in a span of twenty days.

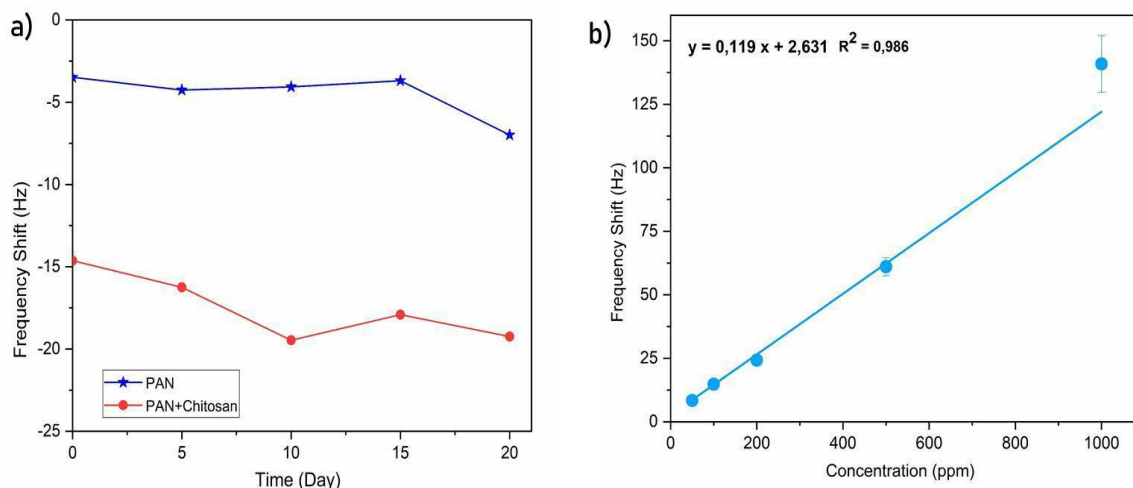


Figure 5. a) PAN sensor stability and a PAN-Chitosan sensor for 20 days; **(b)** The linearity of the sensor to the analyte of safrole.

From Figure 5(a) shows that the response of the PAN nanofiber sensor was varied from 3.48 – 6.99 Hz and the PAN-Chitosan sensors in varied from 14.63 to 19.24 Hz underexposure of 200 ppm safrole vapor. It shows that both QCM sensor is stable for measurement after twenty days used. One that affects the stability of the sensor is the experimental set-up of flushing nitrogen per sampling data. Fig. 5(b) shows the QCM sensor response with a 123.15 Hz PAN-Chitosan membrane for maximum concentration at 1000 ppm. QCM sensor shows almost linear response with five concentration increase, maximum frequency shift reaches 123.15 Hz with regression coefficient R^2 is 0.986.

One of the most important characteristics of a sensor is reviewed for its selectivity. The selectivity of QCM coated by PAN-Chitosan was tested by evaporating the different analyte with predetermined concentration of 200 ppm. Some analytes used to compare the response to safrole are benzene, acetone, ethanol, toluene, and xylene. The response of each analyte is shown in Fig. 6 The graph showed the comparison of the response of each analyte and it shows that the highest response is the safrole whose frequency shift is quite far compared to the other reach 19.2 Hz. Meanwhile the other analytes have response less

than 5 Hz. This shows that the PAN nanofiber modified chitosan was selective for detecting of safrole vapor.

It can be seen from Figure 6 that the modified sensor has high selectivity to the safrole analyte compared with another analyte. Thus, this sensor can be used to detect safrole vapor. the selectivity of the PAN-Chitosan sensor may be considered for developing a safrole gas sensor. However, for further applications need to be studied in more detail related to the mechanism of modification of PAN nanofiber modification and chitosan related to safrole chemical properties.

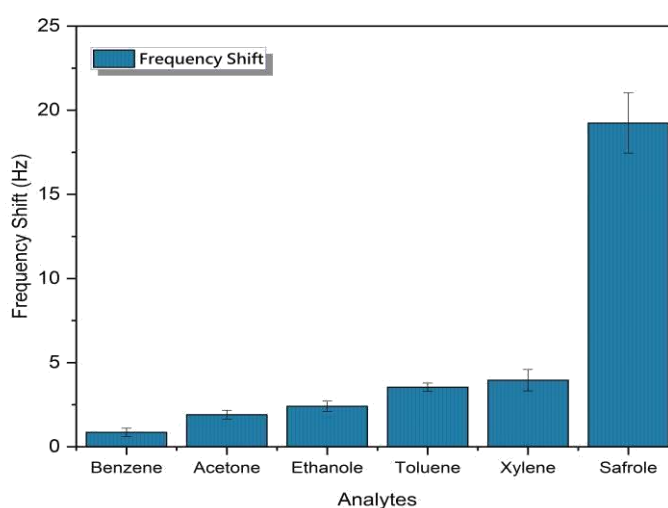


Figure 6. Response of PAN-Chitosan sensor for different gases at a fixed concentration of 200 ppm.

To explain the kinetic adsorption process of the safrole vapor molecule on the PAN-Chitosan QCM sensor, it can use the Langmuir's adsorption equation. Based on this equation (A.K. Havare. et al, 2012), it shows that the time variation to the frequency change resulting from the gas molecule adsorption process can be explained by the following equation:

$$\Delta f(t) = \Delta f_{\max} K' (1 - e^{-k_{\text{obs}} t}) \quad (2)$$

where Δf and $\Delta f_{\max}$ are the resonance frequency shift in QCM, k_{obs} is the inverse of the sensor response time and is a constant. The frequency shift is

comparable to the proportion of the adsorbed mass on the surface of the QCM gold electrode, the frequency shift over time can be fitted using Langmuir's isothermal adsorption equation. By using the Sauerbrey equation, the adsorbed mass changes in the PAN-Chitosan surface layer against the safrole vapor molecule Δm can be described using the equation:

$$\Delta m = \Delta m_{\infty} (1 - e^{-t/\tau}) \quad (3)$$

with Δm_{∞} is the amount of safrole adsorbed on the PAN-Chitosan surface of $t \rightarrow \infty$ and τ is the sensor response time. By using the fitting in equation (3), the response time of QCM coated by PAN-Chitosan when exposed to safrole vapor with a concentration of 200 ppm is $\tau = 40$ s with a frequency shift of 11.48 Hz, shown in Figure 7.

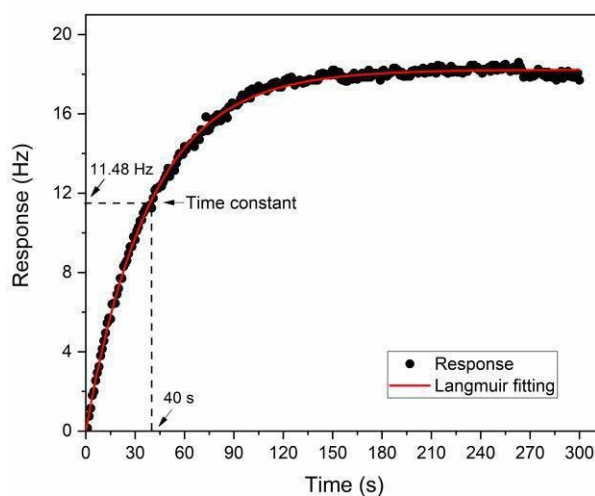


Figure 7. Response time sensor QCM based on PAN-Chitosan

CONCLUSION

We have successfully developed safrole sensor by coating QCM electrodes with electrospun PAN nanofiber followed by modifying with chitosan. The role of chitosan in increasing the sensitivity of the sensor to safrole is significant, i.e. from 0.018 Hz/ppm (without chitosan) to 0.119 Hz/ppm (with additional chitosan). The response (or frequency shift) of the sensor showed linearly increased by the addition of safrole concentration. In addition, the sensor has

good selectivity to distinguish safrole as evidenced by the higher response when examined with other analytes, while the response time of the sensor was 40 seconds. Moreover, the sensitivity of the sensor exhibited quite stable and repeatable for 20 days of measurement.

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