An Enhanced Safrole Sensing Performance of a Polyacrylonitrile Nanofiber-Based-QCM Sensor by Overlaying with Chitosan

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ABSTRACT

We report on a method to enhance the sensing performance of polyacrylonitrile (PAN) nanofiber-based QCM sensor overlaid with chitosan. The PAN nanofibers were deposited on the QCM sensing surface by electrospinning technique followed by overlay with chitosan by a drop-casting method. The Fourier transform infrared (FTIR) spectra confirm that chitosan covers the PAN nanofibers. The SEM images show the average diameter of the produced PAN nanofibers was 236 nm, and it increased to 283 nm after overlay with chitosan. The modified QCM sensor has the sensitivity of 18.7 Hz mg⁻¹ L⁻¹, which is better than that of PAN nanofiber alone of 4.5 Hz mg⁻¹ L⁻¹. It is an increase nearly 5 times. The analytical parameters of the limit of detection (LOD), sensitivity, a time constant, and stability improved after the PAN nanofiber sensor was overlaid with chitosan. The amine groups present in chitosan interact effectively with safrole, thus increase the sensing response. The proposed device is robust, inexpensive, and convenient for detecting safrole, and can be used as an alternative to those of classical instrumental methods for the analysis of safrole as a drug precursor.

Keywords: Chitosan; ecstasy; quartz crystal microbalance; safrole; vapor sensor

INTRODUCTION

In recent years, drug abuse has grown rapidly and become one of the major health threats to our society, causing economic and political issues (Hernández et al. 2014; Singer 2008). The smuggling of unlawful drugs has also spread worldwide. Since 2010, the quantity of drugs seized globally has averaged approximately 4–5 tons per year (United Nations Office on Drugs and Crime 2017). The detection of illegal drug precursors remains a problem faced by law enforcement worldwide. Several studies have highlighted the need for the development of a better method for the detection of drug-synthesis reactants (Hackner et al. 2013; Pinalli et al. 2013). Main drug precursors include benzodioxol, benzyl methyl ketone (BMK), and safrole. Safrole is the precursor for the synthesis of the amphetamine-type stimulant (ATS) drug, N-methyl-3,4-methylenedioxyamphetamine (MDMA), commonly known as ecstasy.

Conventional methods of analyses such as liquid chromatography (LC), gas chromatography (GC), and liquid chromatography coupled with mass spectrometry (LC-MS) (Honeychurch 2016; Saito et al. 2011) are often employed for forensic safrole testing. However, these methods are costly, not portable, and challenging to operate in real-time applications. Therefore, a rapid, reliable and real-time safrole sensor is needed.

Studies show that the development of real-time sensors for volatile organic compounds (VOCs) is progressing rapidly. These sensors are developed based on unique electrode-analyte interactions such as resistive (Wang et
al. 2017), photoelectric (Aba et al. 2014), amperometric (He et al. 2014), optical (Evyapan et al. 2016), and acoustic wave interactions (Wang et al. 2015). To obtain sensitive, real-time, and convenient vapor detection, the quartz crystal microbalance (QCM) sensors are developed as a very promising alternative to classical detection methods (Julian et al. 2019; Siow et al. 2019). The quartz crystal microbalance is an acoustic wave sensor platform, based on the acoustic-electric effect and are capable of determining even nanogram-level mass changes. By deposition on an appropriate sensing chip, the microbalance responds to specific analytes via a frequency shift, which results from the mass increase caused by sorption of analytes onto the sensing material, according to the Sauerbrey equations (Sauerbrey 1959). Various sensing materials such as polymers (Hidayat et al. 2017; Rianjanu et al. 2019b), metal oxides (Zhang et al. 2018, 2015), and some functional materials (Lu et al. 2015) have been introduced to modify QCM sensors.

Nanostructured materials, especially nanofibers, have been studied primarily for devices for gas or vapor sensing (Ding et al. 2010; Rianjanu et al. 2019a; Sun et al. 2012). Nanofibrous structured materials have a large specific surface area, high porosity, and interconnected porous structures (Chotimah et al. 2016; Mahendra et al. 2018; Rianjanu et al. 2018c), which are advantageous for the development of gas or vapor sensing devices. A gas sensor prepared by nanostructured materials has an increased sensitivity due to the larger specific surface areas of the materials (Jia et al. 2017, 2014). We have reported earlier on a nanoﬁber-based QCM safrole sensor (Rianjanu et al. 2018a). However, the sensitivity was not satisfactory. There have been several nanofiber modification methods proposed to increase the sensitivity of nanofibrous sensors, including the construction of a nanofibers–net–binary (NNB) structure (Wang et al. 2014) and the functionalization of the nanofiber (Huang et al. 2013; Jia et al. 2016). The increase in the specific area and chemical functionalization of the QCM sensing chip improves both selectivity and sensitivity.

Electrospun polyacrylonitrile (PAN) nanofibers are mechanically stable, water-insoluble, and hydrophobic, which makes them good candidates for QCM sensing chip modification (Rianjanu et al. 2018b, 2018d). The development of PAN nanofiber as safrole sensor has been done previously (Rianjanu et al. 2018a). Although the methods are easy to use and inexpensive, the sensitivity was insufficient. To increase its sensitivity, we used chitosan to overlay its surface to exploit its amine group. Chitosan (Cs) is a natural polymer which consists of a polysaccharide containing the functional groups −OH and −NH2 and possesses many promising properties such as excellent film-forming ability, high mechanical strength, biodegradability, biocompatibility and antibacterial properties (Ayad et al. 2014). Considerable efforts have been devoted to devising gas/vapor sensors using chitosan and its composites as active layers (Ayad & Minisy 2016; Triyana et al. 2018; Zhang et al. 2017). However, to the best of our knowledge, there has been no effort to develop a promising strategy to modify PAN nanofibers with chitosan and combine these with QCM to construct sensitive safrole sensors.

In this work, we aim to improve the PAN nanofiber-based QCM safrole sensor performance by overlay with chitosan. PAN/Cs nanofibrous membranes’ large surface areas, high porosity, and rigidity of PAN, along with the presence of amine groups in the chitosan structure, cause the QCM sensing chip to exhibit better performance in terms of fast response, reproducibility, and sensitivity, which is promising for routine safrole detection at room temperature.

**MATERIALS AND METHODS**

**MATERIALS**

Polyacrylonitrilite (Mw = 150,000 g/mol) and chitosan (Mw = 190,000−310,000 g/mol) were supplied by Sigma – Aldrich. The nonionic surfactant Triton X–100, N, N-dimethylformamide (DMF), formaldehyde, acetone, ethanol, H2O, 1−propanol, benzene, toluene, xylene, and acetic acid were purchased from Merck, Germany. Safrole with 96% purity, used as the main analyte, was provided officially by The Indonesian National Police, Jakarta. The AT−Cut QCM sensors with gold (Au) electrodes and 10 MHz base resonant frequency were purchased from OpenQCM, Novaetech, Italy. All chemicals were used without any further purification.

**NANOFIBER PREPARATIONS**

Polyacrylonitrilite (PAN) nanofibers were prepared by an electrospinning technique, using conditions similar to those of our previous study (Rianjanu et al. 2018a). After the PAN nanofibers were successfully deposited on the QCM surface, the nanofibers were modified with chitosan by a drop-casting method. The chitosan solution was prepared by dissolving 1.05 g chitosan powder into 10 mL of an aqueous solution of 2 wt. % acetic acid, followed by mechanical stirring at 1000 rpm for 2 h. The 0.01 wt. % chitosan solution was made via the dilution of the concentrated solution. The preparation of the PAN nanofiber overlay with chitosan was prepared as the following. Five microfilter chitosan solution (0.01 wt. %) dropped-cast onto the QCM, which has been initially covered with PAN nanofibers, by using a micropipette to give the chitosan-modified PAN nanofiber QCM chip. After the solvent was completely evaporated at room temperature, the QCM chips were dried in the air overnight. For convenience PAN nanofiber overlay with chitosan called PAN/Cs nanofiber hereafter.

The morphology of the nanofibers was analyzed using a scanning electron microscope (SEM, JEOL JSM−6510). The FTIR spectra were collected on an FTIR spectrophotometer (8201PC, Shimadzu). The schematic illustration of the sensor fabrication with the chemical structures of all used materials is shown in Figure 1.
SAFROLE SENSOR CONFIGURATION AND EXPERIMENTAL SETUP

The schematic diagram for safrole vapor analysis by the batch system is available in our previous work (Rianjanu et al. 2018a; Triyana et al. 2018). The QCM sensor was installed in the testing chamber with a volume of 1.25 L. The measurement was taken place at an ambient condition. The temperature and the relative humidity inside the chamber were monitored by a calibrated sensor of Sensirion SHT-31. Two types of microliter syringes (10-μL, Hamilton Model 701 RN SYR, and 1-μL, Hamilton Model 7001KH SYR) were used for analyte injection. The concentration of the injected analyte in the chamber was expressed in mg·L⁻¹ and calculated using density, percent purity, and volume of analytes. The responses of the QCM sensors were examined by measuring the change in the resonance frequency, as measured by a frequency counter. The change in the resonant frequency of the QCM sensor is related to the change in mass loading on the QCM sensor chip. The frequency change data were recorded with a PC equipped with the LabVIEW graphical programing language. To desorb the analyte vapor from the QCM sensing chips, the dry ambient air was used for purging. The frequency shift of the QCM before and after coating with PAN nanofibers was approximately 1800 Hz. Moreover, after chitosan drop-casting and drying, an additional frequency shift of 1500 Hz was observed. This frequency shift represented the coating on top of the QCM substrate.

RESULTS AND DISCUSSION

NANOFIBER MORPHOLOGY

Figure 2 shows the microscopic view of the PAN nanofiber and PAN/Cs nanofiber at different magnifications. The electrospun PAN nanofibers exhibit randomly oriented three-dimensional (3D) porous structures, with a diameter of approximately 236 ± 46 nm. After chitosan drop-casting and drying (PAN/Cs nanofiber), the nanofiber diameter increased slightly, to 284 ± 29 nm. It indicates that chitosan covers the PAN nanofiber surface. It also confirms that
the 3D structure of the sensor remains unchanged after modification, where the surface of the sensor is covered with chitosan.

**FTIR ANALYSIS**

The FTIR spectra of chitosan powder, PAN nanofiber, and PAN/Cs nanofiber are shown in Figure 3. The sharp bands at 2931 cm\(^{-1}\) and 2877 cm\(^{-1}\) can be attributed to stretching vibrations of ethylene, CH\(_2\), while that at 2245 cm\(^{-1}\) is due to the stretching of C=O. Moreover, the peaks at 1450, 1357, and 1249 cm\(^{-1}\), respectively, correspond to the bending vibrations of various aliphatic C–H groups (CH, CH\(_2\), and CH\(_3\), respectively). A weak peak at 1620 cm\(^{-1}\) could be assigned to amide groups (Ciupradi et al. 2016; Li et al. 2013). Also, the band observed near 1110 cm\(^{-1}\) is possibly due to the C–H rocking mode of CH\(_3\) groups of any residual DMF solvent (Portaccio et al. 2015). The peak that appeared at 1581 cm\(^{-1}\) is likely due to the O–H bending of chitosan’s primary amine. Other peaks of chitosan. The peak at 1581 cm\(^{-1}\) may be attributed to the C=O stretching of the amide groups of chitosan. The peak at 1581 cm\(^{-1}\) is due to the N–H bending of chitosan’s primary amine. Other peaks of chitosan in the fingerprint area are also observed (Ayad et al. 2014; Kim & Lee 2014).

The strong, broadband observed at 3425 cm\(^{-1}\) can be attributed to the stretching vibrations of O–H and N–H groups. The peaks are seen at 2924 cm\(^{-1}\) and 2877 cm\(^{-1}\) could be assigned to the C\(_{sp^3}\)–H stretching of the ethylene groups of chitosan. The peak detected at 1651 cm\(^{-1}\) may be attributed to the C=O stretching of the amide groups of chitosan. The peak at 1581 cm\(^{-1}\) is due to the N–H bending of chitosan’s primary amine. Other peaks of chitosan in the fingerprint area are also observed (Ayad et al. 2014; Kim & Lee 2014).

The FTIR spectra of PAN/Cs nanofibers show the characteristic peaks of both PAN and chitosan. The peaks observed in the PAN/Cs nanofiber FTIR spectra are close to those in the spectrum of PAN nanofiber. The peak detected at 3625 cm\(^{-1}\) is attributed to the N–H stretching of the amine groups of the chitosan confirm the overlay. The peak of O–H bending of chitosan shifted slightly from 1620 to 1627 cm\(^{-1}\). The peaks near 2900 cm\(^{-1}\), attributed to ethylene, do not shift much.

**SAFROLE SENSING PROFILE**

Figure 4(a) shows the frequency response of the as-prepared QCM sensor to safrole vapor. The safrole concentration was varied between 0.3 and 6 mg L\(^{-1}\). Upon safrole injection into the sensing chamber, the frequency shifts sharply in the first few seconds and becomes steady after about 120 s. The PAN nanofiber QCM sensor produces shifts of 1.5, 3, 8, 17, and 33 Hz after being exposed to safrole at concentrations of 0.3, 0.6, 1.2, 3, and 6 mg L\(^{-1}\), respectively. Meanwhile, the PAN/Cs nanofiber QCM sensor produces shift up to 8.5, 14, 25, 60, dan 113 Hz when exposed at a similar concentration. Upon being exposed to safrole at a concentration of 6 mg L\(^{-1}\), the PAN/Cs shows a frequency shift of 113 Hz. At the same concentration, the PAN nanofiber sensor alone exhibits a frequency shift of only 33 Hz. The PAN/Cs nanofiber sensor gives a frequency shift nearly 5-fold larger than that of PAN nanofiber. These results indicate that additionally coating the PAN nanofiber with chitosan improves the QCM response.

The response value of PAN nanofiber and PAN/Cs nanofiber sensor to safrole in the concentration range of 0.3 - 6 mg L\(^{-1}\) is displayed in Figure 4(b). The frequency change is linear with safrole concentration with a determination coefficient (R\(^2\)) of 0.999 for both PAN nanofiber and PAN/Cs nanofiber. The sensitivity of the PAN nanofiber, as calculated from the slope of the plot of frequency shift versus safrole concentration, is 4.5 Hz mg\(^{-1}\) L. Meanwhile, the sensitivity of the PAN/Cs nanofiber is 18.7 Hz mg\(^{-1}\) L. The sensitivity of the PAN/Cs nanofiber sensor nearly 5 times higher than that of PAN nanofiber. The sensitivity of the QCM safrole sensor increases significantly after further overlay with chitosan.

The limit of detection (LOD) and the limit of quantification (LOQ) can be determined based on the standard deviation of blank measurements and the slope of the plot of the frequency shift versus analyte concentration of Figure 4(b) (Long & Winefordner 1983). The LOD and LOQ may be expressed as 3.3 \(σ/S\) and 10 \(σ/S\), respectively, where \(σ\) is the standard deviation of the blank air measurement (0.17 Hz), and \(S\) is the slope of the calibration curve (4.5 Hz and 18.7 Hz mg\(^{-1}\) L). The calculated LOD and LOQ of PAN/Cs nanofiber sensor are found to be 0.03 and 0.09 mg L\(^{-1}\), respectively, while the previous study shows LOD of 1 mg L\(^{-1}\) (Rianjanu et al. 2018a).

Figure 5(a) shows the reproducibility of PAN and PAN/Cs nanofiber as safrole sensors. When the response reaches equilibrium, the fresh dry ambient air was introduced to the detection chamber to flush any absorbed safrole until desorption was complete. The sensor was again exposed to the safrole vapor with the same concentration as before. It appears that the analyte adsorption-desorption cycles are reproducible. The frequency reading returns to its original value after purging the sensor chip with dry fresh air for both sensor chips. The sensing response was considerably reproducible after three consecutive sample injections. This is indicative that the QCM sensing system is reproducible for safrole vapor detection.
short for the rapid detection of the analyte. Our previous study (Rianjanu et al. 2018a) on safrole detection by QCM showed a response time of about 300 s. Long-term stability is important for the applications of gas sensors. The PAN and PAN/Cs nanofiber sensors were regularly tested with 1.2 mg L\(^{-1}\) safrole vapor for 30 days to evaluate their long-term stability. During this period, each QCM chip was used to measure the analyte once every 5 days. Figure 7 displays the frequency shift as a function of time over 30 days. The first response is relatively stable.

To investigate the repeatability of the PAN and PAN/Cs nanofiber sensor, the sensor was exposed repeatedly to safrole vapor at a fixed concentration of 1.2 mg L\(^{-1}\). When the QCM frequency reading reached equilibrium after each safrole injection, the prepared sensor was purged with dry ambient air to remove adsorbed safrole molecules. Figure 5(b) shows the QCM sensing repeatability test. The standard deviations for PAN and PAN/Cs nanofiber-based sensors were found to be 0.4 Hz and 1.7 Hz, respectively. The small fluctuation in the frequency shift suggests that both QCM sensing chips show good repeatability. Moreover, the relative standard deviation (RSD) was calculated to be 8.2% and 7.5% for PAN nanofiber and PAN/Cs nanofiber sensor, respectively. The small relative standard deviation for PAN/Cs nanofiber sensor shows the chitosan-overlaid PAN film improved the sensor repeatability.

Figure 6 shows the frequency response of the PAN and PAN/Cs nanofiber sensor to safrole vapor at 1.2 mg L\(^{-1}\). It is fit for the first-order instrument response. The time constant (\(\tau\)), defined as the time needed for an instrument to achieve 63.2\% of its maximum response value, is 35 and 51 s for PAN nanofiber and PAN/Cs nanofiber sensor, respectively. It is shown that PAN nanofiber overlay with chitosan exhibit faster time constant than that of PAN nanofiber. It also confirms the improvement of sensing performance after chitosan overlay. The instrument response time must be
after 30 days of measurement for the QCM chips, indicating the long-term stability of the QCM system. The maximum frequency fluctuation is about 0.9 Hz (15%) and 2.6 Hz (11%) for PAN nanofiber and PAN/Cs nanofiber sensor, respectively. The result indicates improved long-term stability after chitosan overlay.

The PAN/Cs nanofiber sensing system towards 1.2 mg L\(^{-1}\) of various VOC gases, which usually present in the air (US EPA), was investigated, and the results are shown in Figure 8. The highest frequency shift has been observed as 25.66 Hz for safrole sample. The other frequencies shifts were observed much lower compared to that of safrole. Thus, it can be concluded that the PAN/Cs nanofiber sensor showed an excellent response to safrole vapor.

THE PROPOSED GAS SENSING MECHANISM

Based on the safrole sensing properties of the PAN/Cs nanofiber, we believe that the nanostructured nature of the sensing surface is critical. The porous structure of the PAN/Cs nanofiber is advantageous to achieve quick and large frequency responses. The analyte vapor is effectively diffused into the nanofibers. A large frequency shift serves as evidence of a strong interaction between nanofibers and analytes. We believe that the intermolecular forces between the nanofibers at the QCM electrode surface and safrole are the major contributors to the frequency response.

Figure 9 depicts the proposed intermolecular interactions between PAN/Cs nanofiber and safrole vapor. Each chitosan subunit has an amine group that contains a nitrogen atom. This nitrogen atom has one lone pair of electrons and can act as a Lewis base. As proposed in the previous study (Rianjanu et al. 2018a) the frequency shift is due to a strong hydrogen bond between the hydrogen atoms of safrole and the nitrogen atom at the chitosan subunit. The two hydrogen atoms located between two oxygen atoms in the safrole structure will be electron-deficient, thus behaving as Lewis acids. The significant frequency changes caused by the strong intermolecular bonding between the...
nitrogen and hydrogen atoms. Other weak intermolecular interaction such as hydrophobic–hydrophilic, dipole-dipole, and π–π interactions may also occur. Moreover, other tested VOCs showed weaker intermolecular interaction compared to safrole, indicate by lower frequency changes (Figure 8).

The other possibilities are that the chitosan does not adequately cover the PAN nanofiber surface. Part of the PAN fibers may interact with safrole by intermolecular force as we reported earlier (Rianjanu et al. 2018a). However, the chitosan fibers still have a significant contribution to the sensing interactions. The nanofibrous structure of both PAN and PAN/Cs nanofiber provides a much high surface area. Moreover, when the PAN nanofibers are overlaid with chitosan, the chitosan molecules cover the PAN nanofiber surface. Chitosan with a significant number of amine groups will interact with safrole by intermolecular interaction. The high surface area of the nanofibers and strong chitosan-safrole intermolecular force is believed to contribute to the increased sensitivity of the PAN/Cs nanofiber sensor. The PAN nanofibers alone can also interact directly with safrole molecule via charge transfer mechanism through their nitrile groups and the safrole’s hydrogen atoms that are sandwiched in between two ether groups (Rianjanu et al. 2018a). When the PAN nanofibers are coated with chitosan, the nitrile groups are less accessible to safrole anymore. It means that PAN is needed to give a nanofibrous coating with the large surface area.

CONCLUSION

Electrospinning and drop-casting methods were used to create a PAN/Cs nanofiber-based QCM sensor for safrole analysis. The 3D structure of the PAN and PAN/Cs nanofibers leads to a good response to safrole. Moreover, the QCM modified with PAN nanofibers overlay with chitosan gives a better response to safrole vapor detection compared to PAN nanofiber alone. The others sensing performance, including the sensitivity, repeatability, time constant, and long-term stability, also shows an improvement when the PAN nanofiber sensor overlay with chitosan. The large response of the QCM was due to the interaction between chitosan’s amine group and safrole through intermolecular hydrogen bonding. It could be very promising for the routine detection of safrole. The QCM sensing chip modified with electrospun polymers may offer a new strategy for real-time sensing methods for precursors of drugs, especially MDMA and other ATS derivatives.

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