Study the Sensitivity of Quartz Crystal Microbalance (QCM) Sensor Coated with Different Thickness of Polyaniline for Determination Vapours of Ethanol, Propanol, Hexane and Benzene

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Abstract

A quartz crystal microbalance (QCM) sensor coated with a thin film of polyaniline was used as a sensitive method for the determination of a number of following vapours: ethanol, propanol, hexane and benzene. The detection was based on the absorption of the vapours of these organic compounds into the film by using gas cell chamber. The detection of these vapours can be obtained in part per million (ppm). The work includes the use of polyaniline films with different thickness (70, 93, 118 and 176) nm where thickness of the PANI films was controlled by the spin coating process. Results show that increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours of ethanol, propanol hexane and benzene. Best sensitivity to ethanol and hexane were obtained with film thicknesses 93nm while in the case of propanol best results were obtained with thickness of 118 and 93 nm. Thickness of 93 and 176 nm gave good sensitivity to benzene.

Keywords: quartz crystal microbalance, polyaniline, film thickness, ethanol, propanol, hexane, benzene.

1. Introduction

Since the quartz crystal microbalance (QCM), was first introduced by Sauerbrey in 1959, it has become a largely used instrument for small mass measurements in vacuum, gas, and liquid phase. On the other hand, the quartz crystal microbalance (QCM), which became a largely used instrument during the last decades, can detect up to 10^{-16} kg (Mecea 2005). Many years ago, the chemical sensors have made great advances and have taken root in human life and industry as a feature of modern technology. In recent years, polymers have found an increasing role in sensorics due to their unique characteristics, and a number of new sensors have been developed (Hosseini et al. 2005). The monitoring of volatile organic compounds (VOCs) has become a serious task due to regulations in many countries of the world. Gas chromatography and infrared spectroscopy require large quantities of samples and are time consuming. Therefore, alternative methods are required (Matsuguchi & Uno 2006). Amongst various types of sensors, there is a considerable interest in QCM (Price et al. 2002). When the surface of a quartz crystal electrode is coated with a sensitive coating, capable of interacting with the environment of interest, it is possible to construct a sensitive sensor to the component under investigation; the selection of sensitive coating is a critical task in the design and performance of chemical QCM sensors (Patel et al. 2000). The mass of the film (m) can be monitored by measuring the oscillating frequency change (Δf) of a quartz crystal and using Sauerbrey equation (Ayad et al. 2008):

$$\Delta f = -\left(\frac{2f_o^2}{\sqrt{\rho_Q \mu_Q}} \right) m$$

Where f_o (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g/cm3) and μ_Q is the shear modulus (2.947×10^{10} N/m^2). Polymers are widely used as chemically sensitive coating materials on quartz crystal electrodes and are particularly suitable for detecting VOCs; because of the ability of the polymer to sorb vapour reversibly (Sun & Okada 2001). The chemical structure and physical properties of polymeric coatings and the nature of interaction between polymer coatings and vapour molecules determine the selectivity, sensitivity, signal kinetics and reversibility of the sensors (McGill et al. 2000). Conducting polymers such as polyaniline (PANI), polypyrrole, and polythiophene have been widely investigated as effective materials for chemical sensors (Matsuguchi et al. 2003). The advantages of conducting polymers compared to inorganic materials used until now are their diversity, their easy synthesis and particularly, their sensitivity at room temperature (Schollhorn et al. 1998). Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors. As a result, more and more attentions have been paid to the sensors fabricated from conducting polymers, and a lot of related articles were published for example polyaniline was found to be a better choice for gases such as ammonia because of its higher sensitivity, reversible response and shorter response time (Sengupta et al. 2011). Wang et al. (2006) studied the sensitivity, short-term

reproducibility, stability, and response time properties of ZnO nanowires-modified quartz crystal as a gas-detecting sensor. Ayad *et al*. (2008) used quartz crystal microbalance (QCM) sensor, coated with a thin film of polyaniline emeraldine base (EB), as a sensitive method for the determination of a number of aliphatic chlorinated hydrocarbons such as carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane vapours. Polyaniline-modified quartz crystal microbalance (QCM) sensor was obtained through immobilizing the polyaniline film on the silver electrode surface of quartz crystal resonator by an electrochemical method and the sensor was studied for detecting the formic acid gas of different concentrations (Yan *et al.* 2012). The aim of the present work was to employ different thickness PANI film coated QCM as a sensor for the following vapours: ethanol, propanol, hexane and benzene.

2. Experimental

Different thickness of PANI films were deposited on both sides of gold electrode of the QCM by using spin coating technique. PANI films obtained were 70, 93, 118 and 176 nm and thickness measurements were achieved by using ellipsometry. Gas cell chamber (controlled by software) was used to measure the sensitivity of QCM when exposed to different analysts of ethanol, propanol hexane and benzene. The QCM was exposed to air after the absorption of each analyte. The backshift of the crystal frequency to its initial value was taken as an indication of full desorption. All measurements were carried out at room temperature. Sensitivity is defined as the ability of a sensor to produce a signal when low concentrations of a target analyte are present. The larger the signal, the more sensitive a sensor is. The sensitivity of a sensing material is defined as the concentration of analyte sorbed onto the sensing material divided by the total concentration of the analyte (Stewart 2011).

Total

3. Result and discussion

Figures 1, 2, 3, and 4 show that increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours of ethanol, propanol, hexane and benzene. This is expected since when more vapor molecules are provided in the test atmosphere, more molecules would be absorbed into the PANI coating on the QCM. After each addition of vapor concentration, the frequency of the crystal was back shifted to its initial value by drying the electrode using air, which indicates full desorption of vapor from the electrode surface. This behaviour confirms that the sensing interaction between the imine and amine sites of PANI chains coating and vapor is a physical absorption through a dipole/dipole interaction or hydrogen bonding. The presence of hydrogen attached to an electronegative nitrogen in all of the polymers allows for hydrogen bonding (Stewart 2011).

Figure 1 shows increasing of sensitivity with increase of the concentration of injected analyte of ethanol. The increase in resistivity of the sensor on exposure to ethanol is thought to be caused by an interaction via H-bonding between the –OH groups of ethanol molecules and the nitrogen atoms of PANI, leading to the hindrance in conformational rearrangements of the macromolecules that impedes electron delocalization and charge transport through the polymer chain (Choudhury 2009). Best sensitivity was obtained with film thicknesses 93 nm. So; it is found that the polymer thickness would affect the sensitivity of the sensor. This can be assigned to the increased active sites of the polymer as the film thickness increases (Mirmohseni & Oladegaragoze 2004). Therefore PANI of 93 nm considered suitable thickness to create active sites and but ethanol molecules only physically absorb on the PANI surface. On the other hand it was found that thickness of 118 and176 nm gave low sensitivity to ethanol as shown in figure 1 due to poor physically absorb on the PANI surface. Figure 2 illustrates the effect of PANI film thickness on sensitivity of QCM with increase of the concentration of injected analyte of propanol. Also it can be seen that with increase in analyte concentration the sensitivity increases, which could be attributed to the interaction via H-bonding between the-OH groups of propanol molecules and the nitrogen atoms of PANI. As shown in figure 2 best results were obtained with thickness of 118 and 93 nm. By comparison figure 1 and 2 it can be seen that QCM, with PANI film of thickness 93 nm, has more sensitivity to propanol because more physical absorption take place. This is because low molecular weight alcohols vapors decrease the conductivity of the PANI faster than higher molecular weight alcohols. These results are in agreement with the literature. For example, Josowicz and Janata (1986) and Bartlett and Chung (1989) observed a much slower response for ethanol vapor when compared to methanol vapor. It was interpreted that the electrons in the PANI were much more tightly bound in the presence of the low molecular weight alcohol. Figure 3and 4 demonstrates behavior of QCM towards increase of the concentration of injected analyte of hexane and benzene respectively which both are non-polar molecular. This would then indicate that polarity is not the only factor in generating a response on the nanosensors (Yang 2010). Elucidation of the exact mechanisms would require extensive research with a variety of substances and possible development of structure activity relationships. Also it can be seen that best sensitivity to hexane was obtained with PANI film thicknesses 93 nm.

Figure 4 shows that thickness of 93 and 176 gave good sensitivity to benzene. It is obvious from figure 3 and 4 that QCM has more sensitivity to benzene compare to hexane.

4. Conclusions

It was found increasing of sensitivity with increase of the concentration of injected analyte when the PANI-film-coated QCM was exposed to the vapours of ethanol, benzene, hexane and propanol. Best sensitivity to ethanol was obtained with PANI film thicknesses of 93 nm. Thickness of 118 and176 nm gave low sensitive to ethanol due to poor physically absorb on the PANI surface. PANI film thicknesses of 93 gave best sensitivity to propanol. Using thickness of 93 and 176 gave good sensitivity to benzene.While best sensitivity to hexane was achieved by using PANI film of thickness 93 nm.

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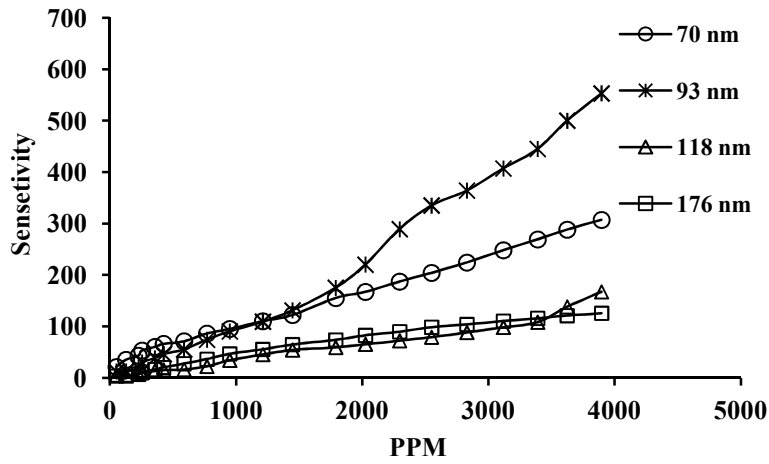
Figure1. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Ethanol
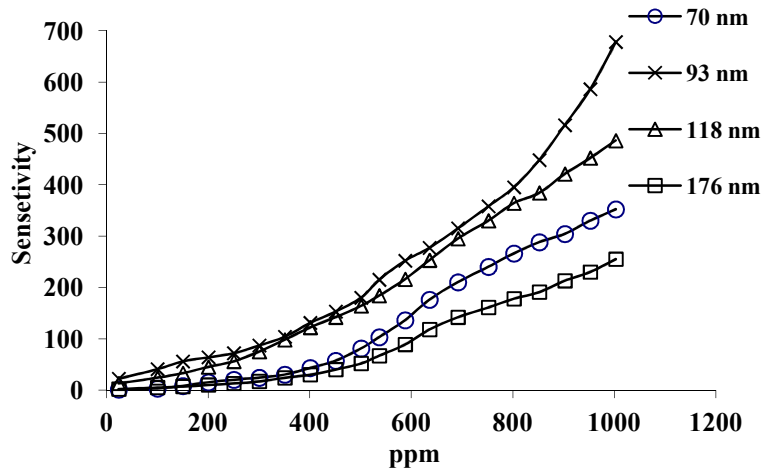

Figure 2. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Propanol
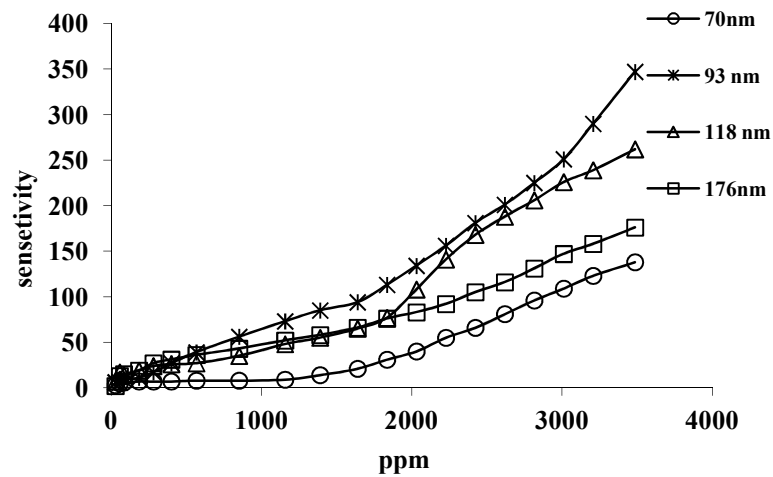

Figure 3. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Hexane
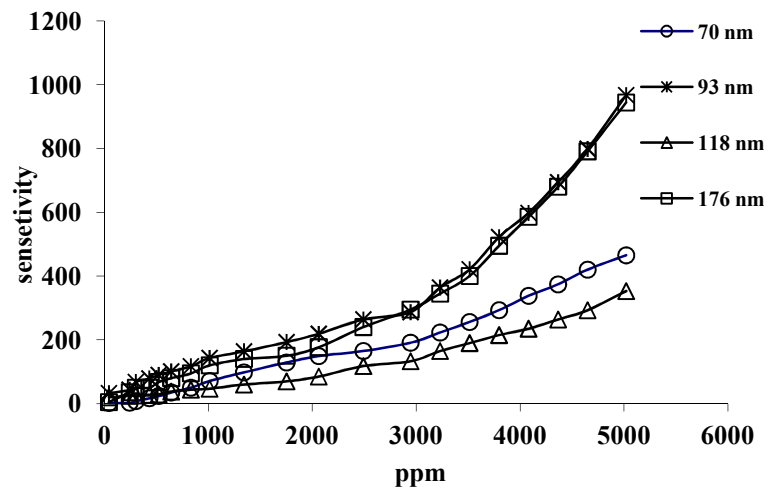
Figure 4. Sensitivity of QCM Coated with Different Thickness of PANI Exposed to Benzene.

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