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Detection and kinetics of methylamine on chitosan film coated quartz crystal microbalance electrode

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ABSTRACT

Chitosan (CHS) coated-quartz crystal microbalance (QCM) electrode was utilized as a sensor for the recognition of methylamine. A homogeneous smooth thin film of CHS coating on the QCM electrode was prepared by the drop casting of CHS solution. The frequency shifts (Δf) of the QCM due to the adsorption of methylamine on the CHS film were measured as a function of concentrations. Calibration curve was plotted which shows a linear relationship of Δf (Hz) versus the methylamine concentrations in the range of 0.5–2.3 mg L^{-1}. In addition to the linearity (R^2 = 0.994) and short response time, the sensor shows a high sensitivity, reproducibility and fast reversibility. The kinetics of methylamine adsorption onto CHS film were calculated. Based on the dynamic analysis of adsorption, the association constant of methylamine vapor molecules with CHS films was estimated to be 11386.3 M^{-1}. The diffusion coefficients of various aliphatic amines were calculated and showed that methylamine exhibits the highest diffusion coefficient value compared to dimethylamine and diethylamine.

1. Introduction

The chemical modification of the quartz crystal microbalance (QCM) electrode by using macrocycles [1–4], mono- and multilayers [5–7] and bio-organic molecules [8,9] has been widely utilized in the detection of toxic gases and organic vapors due to its extreme sensitivity and simplicity. In the gas systems, it is reported that simple dispersion forces, hydrogen bonding, hydrophilicity and dipole–dipole interactions between the sensor coatings and the analytes play an important contribution to enhance the signal intensity of the sensor.

Appropriate coating materials on QCM sensor surfaces have played a crucial role on determining the sensitivity. The production of layers of polymers can be executed by different coating methods e.g. spin coating, spray coating, and drop casting of solutions [10]. Recently, we have utilized polyaniline (PANI) coating on the QCM electrode as a sensor of the pH [11], phosphoric acid [12], chlorinated hydrocarbons, aliphatic amines and alcohols vapor [13–15]. These sensors showed an excellent reproducibility and reversibility. It has been concluded that the hydrophilicity in addition to dispersion forces, hydrogen bonding or dipole–dipole interactions plays an important contribution to enhance the signal intensity of these sensors.

Chitosan (CHS), the organic polymer, bears two types of reactive groups, the free amino groups and the hydroxyl groups. CHS is soluble in acidic aqueous solutions and forms strong films from the solution containing as little as 1 wt% of acetic acid. Furthermore, CHS has many interesting characteristics including good mechanical strength, and low cost [16,17]. These properties were considered so CHS is utilized to coat the QCM electrode to be used as a gas sensor. Recently, CHS film sensor fabricated by an electrochemical deposition technique was used to estimate the acetone concentrations in human's breath, to accurately diagnose diabetes mellitus in patients. The detection was based on the electrical properties of CHS film in the presence of water molecules. Acetone normal vapor concentration in the breath varies from 0.3 to 0.9 ppm at room temperature. This sensor highly performed with a good response, recovery, stability and repeatability [18]. Iron oxide gas sensor was fabricated by coating Fe_3O_4 nanoparticles by CHS. [19] The Fe_3O_4/CHS nanocomposite based sensor had a significantly better gas sensing response toward H_2, CO, C_2H_5OH, and NH_3 gases compared to the pristine Fe_3O_4 based sensor [19]. The same nanocomposite film which was deposited onto indium-tin-oxide (ITO) was utilized for the detection of urea with a good sensitivity [20]. Furthermore, the dispersion of carbon nanoparticles into CHS matrix has been used to build up water, toluene and methanol vapors sensor. The sensor shows ranking vapors

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in the following order: water > methanol > toluene [21]. An optical micro-electromechanical systems sensor for catechol detection was fabricated by utilizing the UV range [22] with a detection limit of 0.2 mM for a 10 min response time.

The sensing of low concentrations of chemical vapors and volatile organic compounds (VOCs) is an important issue with a great interest in various applications. The volatile organic amines vapors are of particular interest since both aliphatic and aromatic amines can induce toxicological responses at low concentrations [23,24].

The present work reports the using of thin CHS films coated the QCM electrode as a sensor for the detection of methylamine vapors. Calibration curve between Δf (Hz) versus the methylamine concentrations has been constructed. The kinetics of methylamine adsorption onto CHS film have been studied. A simple, rapid, sensitive and reproducible sensor has been achieved.

2. Experimental

2.1. Reagents and materials

Chitosan (CHS) of high M wt. (~310,000 to □ 375,000 Da) was purchased from (Sigma-Aldrich, USA). Methylamine 40% solution (LOBA Chemie, India), dimethyl amine 40% solution (Oxford, India), diethyl amine 99% (MERCK, Germany) and glacial acetic acid 99% (ADWIC, Egypt) were used with no further purification.

2.2. Quartz crystal microbalance measurements

An AT-cut 5 MHz quartz crystal with gold electrodes is used. The QCM apparatus used for the frequency measurements was previously described [25]. The resonance frequency of the crystal was determined by GW frequency counter of the model GFC-8055G.

The QCM operation principle is dependent on the resonant frequency shift caused by the adsorption of gas molecules on the coated-sensing films according to Sarerbrey equation [26].

$$\Delta f = -\left(\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}}\right) m' \quad (1)$$

where, f_0 (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g cm^{-3}), μ_Q is the shear modulus (2.947×10^{11} dyne cm^{-2}) and m' is the mass change per unit area.

The gold QCM electrode was cleaned by soaking in piranha solution (3:1, H_2SO_4:30% H_2O_2) for 5 min, followed by the rinsing thoroughly with distilled water. The surface modification of the gold-coated QCM plate was carried out by drop casting of 0.1 ml CHS solution (4 mg ml^{-1} of CHS in 2% v/v acetic acid) on the surface of the QCM gold electrode by micro-syringe). The droplet was spread aided by the tip of the syringe to cover the entire gold electrode. The entrapped gas bubbles in the formed film were removed by putting the quartz crystal in a vacuum desiccator. Then the film was dried by the oven at 50 °C. The surface topography of CHS film was examined by using the scanning electron microscope (SEM) of the model (JEOL, JSM-6340F). SEM image of the CHS film shows the formation of a homogenous and smooth film (Fig. 1).

The thickness of the homogeneous film, L (cm) can be determined through the density (ρ) of the CHS films, $\rho \approx 1.37$ (g cm^{-3}) [27] using the relation:

$$m' = \rho L \quad (2)$$

All measurements were carried out in a double wall vessel supplied with a small fan to get a fast homogeneous atmosphere spontaneously after the injection of the analyte. In order to obtain extremely high oscillation capabilities with very low noise, all the experiments were carried out in a hermetical condition with the usage of a shielding box for impeding the magnetic field, and a set of constant potential was supplied for keeping the voltage stable.

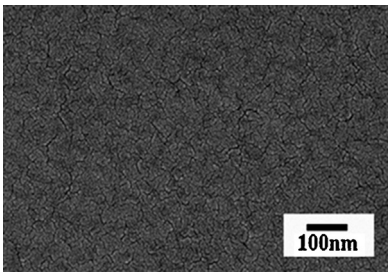

Fig. 1. SEM image of CHS film.

A 5 μl micro-syringe (Perkin Elmer, Australia) was used for the analyte injections. The concentration of the injected VOCs was calculated in mg L^{-1} by using its density, purity percent and the injected volume.

After the recognition of the analyte, the CHS thin film coating on the QCM gold electrode is exposed to hot dry air to desorb the analyte and recover the sensor. The backshift of the crystal frequency to its initial value was taken as an indication of the full regeneration.

3. Results and discussion

The CHS film coating on the electrode of QCM was exposed to different concentrations of methylamines' vapors. The frequency changes due to the adsorption of methylamine vapor onto the film as a function of time were recorded.

Fig. 2(a) shows the time dependence of experimental QCM frequency shifts due to the adsorption of different concentrations of methylamine vapor when exposed to the CHS film coated QCM electrode (film thickness of 790 nm). The frequency of the quartz crystal decreased due to the adsorption of the vapors onto the polymer film according to Eq. (1). Δf increased linearly with the increasing of the concentration of the tested methylamine vapor. Since more methylamine molecules were provided in the test atmosphere, more molecules were expected to be adsorbed onto the CHS film coating on the QCM electrode. The equilibrium was shown to be attained in less than one minute which indicates the high sensitivity of CHS film towards methylamine molecules.

After the equilibrium has been attained, the sensor can be recovered by drying the electrode using hot dry air. The response obtained from the sensor should be linear against the concentrations of the methylamine vapors. Thus, a calibration curve of achieved Δf versus different concentrations of methylamine vapors ranged from 0.5–2.3 mg L^{-1} was plotted as shown in Fig. 2(b). A linear relationship was obtained with a correlation coefficient (R^2) and slope (sensitivity) of 0.994 and 305.9 Hz mg^{-1} L, respectively.

3.1. Adsorption kinetics

The time-dependent frequency data can be used to study the adsorption kinetics [28]. The decrease in the resonance frequency represents the adsorption process. The time-dependent variation of mass of the adsorbed vapor molecules on the CHS film surface (Δm_t) can be defined as following:

$$\Delta m_t = \Delta m_\infty (1 - e^{-t/\tau}) \quad (2)$$

Using Sauerbrey relation given in Eq. (1),

$$\Delta m = -C\Delta f \quad (3)$$

so, Eq. (2) can be expressed as following:

$$\Delta f_t = \Delta f_\infty (1 - e^{-t/\tau}) \quad (4)$$

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