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Aging effect of a molecularly imprinted polymer on a quartz tuning fork sensor for detection of volatile organic compounds

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ABSTRACT

The sensing stability and sensitivity of a molecularly imprinted polymer (MIP) selective to the adsorption of hydrocarbons was studied. The MIP was deposited on a quartz crystal tuning fork (QTF) resonator, whose chemical and physical properties were monitored over time, using Scanning Electron Microscopy (SEM), Brunauer–Emmett–Teller adsorption isotherm analysis (BET), and Fourier transform infrared spectroscopy (FTIR). In addition, kinetic binding analysis of the MIP-modified QTF sensor was carried out for the sensors stored and operated under ambient conditions (740 mmHg, 20–23 °C). Although the polymer was able to maintain its physical and chemical properties at microscopic, BET adsorption, and spectroscopic levels, the intrinsic adsorption properties of hydrocarbons onto MIP binding sites altered over time, which suggest that the 3-D conformational changes of the polymer binding sites occurring at nanoscopic/angstrom level may cause the sensitivity degradation in MIP. The changes were significantly reduced by stabilizing the polymer under low storage temperatures.

1. Introduction

Volatile organic compounds (VOC) are organic chemicals emitted from anthropogenic and biogenic sources with significant vapor pressure [1,2]. According to the United States Environmental Protection Agency (EPA), VOCs are one of the major pollutants for indoor and outdoor air quality since they are emitted from furniture, appliances, and construction materials as well as incomplete combustion of fuels (cars, trucks). Most of VOCs are harmful to health, especially the respiratory system [3], and therefore, there is a need of determining personal exposure concentrations. Along this line, a plethora of analytical methods have been developed to monitor VOC concentrations. Among them, the most popular ones are photo-ionization detection (PID) and gas chromatography–mass spectrometry (GC–MS). In addition, other detection methods have been created and used to supplement GC, such as thermal conductivity (TCD) [4], differential mobility (DMD) [5], and flame ionization (FID) [6].

PID has been particularly useful due to its portability. The gas sample is exposed to UV light (usually with an energy level of 10.6 eV) [7], and VOCs are ionized due to the loss of electrons. The positively charged ions impact onto an electrometer, generating a current, which is then amplified and converted into a concentration value for display. There have been many patents regarding gas detection with PID [8–10]. Due to the nature of detection, some non-VOC gases are also detected by PID [11,12], and therefore the context of use is relevant for PID technology applications. GC–MS is the gold standard in gas detection. It has been widely used in environmental monitoring and cleanup, law enforcement [13], and many other applications [14]. The sample gas components are first separated before a mass spectrometry detector is used to identify and quantify each individual chemical concentration based on different mass-to-charge ratio. GC–MS is very accurate, and a well-established technique for laboratory-based analysis. However, the bulky instruments have very limited applications in monitoring personal assessment. For the need of personal exposure monitoring, some personal VOC monitors have been recently developed [15]. One example is a wearable wireless monitor developed by our group. The monitor is based on quartz crystal tuning forks (QTF) sensors for environmental VOCs [16–18]. Similar to QCM resonator,

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quartz tuning forks are mass sensitive resonators useful in biosensors [19,20]. In the wearable wireless monitor, the QTF sensors are coated with polymer films that are sensitive and selective to target VOCs. For instance, molecularly imprinted polymers (MIP) are highly selective to hydrocarbons, which are carcinogens or potential carcinogens. The molecularly imprinted polymers are formed in the presence of a specific molecule template that is extracted afterwards, leaving binding site complementary cavities with chemical affinity to the molecules similar to the original molecule template or its family [21].

Many studies have been done on the molecularly imprinted polymer structure [21], including thermal stability [22], and chemical and physical adsorption calculations and evaluations [23–25]. However, there are no former systematic studies of MIP aging. For the first time, this work demonstrates evidences of MIP aging and its effect on MIP sensing properties. We have built MIP-modified QTF sensors, and systematically tested the stability of the material. MIP is a porous and adsorptive sensing material [26–28], and we have observed an interesting aging effect on the sensing material with a concomitant decay of sensor sensitivity over time. To better understand the adsorption/desorption kinetics and physical/chemical transformation of the MIP, we have investigated the structural changes in the polymer, as well as the number of selective binding sites using several techniques. We have also studied the stability of MIP-modified QTF sensors under real operative conditions, and proposed a mechanism behind the sensitivity degradation. With the ultimate goal of achieving sensitive and stable sensor with long shelf-time, we have explored a solution to minimize the sensitivity degradation in MIP.

2. Material and methods

2.1. Quartz tuning fork sensors

The QTFs are piezoelectric crystal resonators with high mass sensitivity, thermal and mechanical stability, and self-sensing capability [29]. The QTF sensors used in the present experiments have a native resonant frequency of 32.768 kHz and a dimension of 4 mm × 0.6 mm × 0.35 mm (manufactured by Jiangcheng Electronic Limited Company), which renders a mass sensitivity of 20 ng/mm^2.

2.2. Molecularly imprinted polymer (MIP) coated QTF sensors

2.2.1. Polymer preparation

The MIP is synthesized using divinylbenzene (mixture of o-, m-, p-, Sigma Aldrich) as both monomer and cross-linker, o-xylene (Sigma Aldrich) as both template and solvent, and azobisisobutyronitrile (AIBN, Sigma Aldrich) as initiator, under argon environment, 85 °C, and overnight. In addition, MIPs using styrene (Sigma Aldrich) and the above mentioned components were synthesized to study the effect of the ratio of monomer (styrene)-to-cross-linker (divinylbenzene) on the sensitivity of the polymer to xylene.

2.2.2. Polymer treatment and QTF sensor coating

After synthesis, the polymer is broken into smaller pieces (estimated size: 1–5 mm) first and smashed using ball milling machine (PQ-NO 4 Planetary Ball Mill, Across International) to obtain consistent particle size. The uniform polymer particles (estimated size: 1–10 μm) are then dispersed in o-xylene solvent and the mixture is casted onto QTFs with a metal needle syringe. An optical image of a modified QTF sensor is shown in Fig. 1.

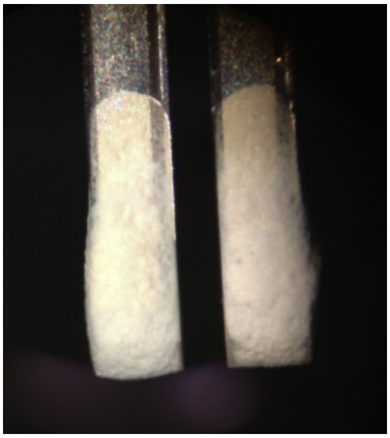

Fig. 1. A MIP modified QTF sensor.

2.3. Adsorption–desorption kinetics and sensitivity studies

In order to study the adsorption–desorption kinetics and sensitivity, we used a wireless personal monitor, which consists of four functions: (a) Collection and Delivery: the air sample is collected and delivered via an alternating valve-activated mechanism with a purging channel and a sampling channel. In the purging channel, particulates and VOCs from air are filtered out with a zeroing filter for 120 s, producing a particulate and VOC-free air sample that is used for baseline assessment of the MIP-modified QTF sensors. In the sampling channel, particles in the sampled air are filtered out, producing a 60 s sample for testing hydrocarbons. Before entering the sensing chamber, sample gas will pass through a Nafion tube for humidity balancing. (b) Sensing and Detection: after the air sample is produced, it passes a sensor chamber with a MIP-modified QTF sensor, and an unmodified QTF that serves as a reference sensor. The two QTF sensors are placed in-line along the flow direction for detection, and the differential sensing signal between the MIP-modified QTF and unmodified QTF sensor is assessed. (c) Converting chemical binding events to a readable electronic output: the resonant frequency shifts of QTF sensors upon changes in its mass, which thus allows us to detect the mass change due to the adsorption of molecules in MIP by measuring the frequency shift. (d) Data transmission and signal processing: the differential sensor signal is transmitted to a recording system via Bluetooth®, where the signal is captured as raw signal, and further processed as concentration output. The recording system is a custom-designed application used on a smart phone, which helps and supports users to assess instantaneous concentration readings.

In this paper, we define sensor response as the resonant frequency shift on QTF sensors after the 1 min period of sampling.

2.4. Calibration curve

Using the above-described setup, we obtained the calibration curves with differential sensor signal of frequency (Δf/Hz) under different concentrations of gas samples, including 0 ppm (clean air), 1 ppm, 20 ppm, 40 ppm, 80 ppm, and 160 ppm. O-xylene was chosen as the model analyte. Air samples were prepared in laminated bags with clean and dry air balance. All air samples' concentration were also monitored using PID as a reference. Tests were processed under ambient conditions on the first day and 30 days after the sensor was prepared. During storage period, the sensors were kept under ambient condition undisturbed. In addition, the response of the MIP-modified sensor stored at ambient conditions was monitored for consecutive days at normal pressure and temperature conditions (740 mmHg and 20–23 °C).