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Nanofibrous polyethyleneimine membranes as sensitive coatings for quartz crystal microbalance-based formaldehyde sensors

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ABSTRACT

A novel formaldehyde sensor was fabricated by electrospinning deposition of nanofibrous polyethyleneimine (PEI)/poly(vinyl alcohol) (PVA) membranes as sensitive coatings on quartz crystal microbalance (QCM). The morphology of the porous three-dimensional PEI/PVA membranes comprising fibers with diameter of 40 nm to 1.8 μm was controllable by tuning the compositions of polymers and solvents in PEI/PVA solutions. The resultant sensors showed a fast response to formaldehyde and a linear relationship upon increasing the formaldehyde concentrations due to the reversible interaction between formaldehyde molecules and amine groups of PEI. The sensor responses were reversible and reproducible towards formaldehyde in the concentration range of 10–255 ppm at room temperature. The sensitivity of fibrous membrane coated QCM sensors formed from the cosolvent of water and ethanol was three times higher than that of corresponded flat membrane coated QCM sensors when exposed to 255 ppm of formaldehyde. Relative humidity in testing chamber was proved to be the key parameter to affect the sensor sensitivity. Additionally, the fibrous PEI/PVA membrane coated QCM sensors exhibited a good selectivity to formaldehyde when tested with competing vapors.

1. Introduction

Since Sauerbrey [1] published the pioneering literature on experimental verification of the mass–frequency shift relation for quartz crystal resonators, the quartz crystal microbalance (QCM) has been established as a reliable technique to detect small mass changes of even smaller than nanogram order when used as chemical-vapor-deposition thickness probes and chemical microsensors [2]. Up to now, a variety of materials such as metals, ceramics, polymers, self-assembled monolayers, dendrimers, lipids, and waxes [3,4], have been employed as sensitive coatings on QCM to improve the sensor sensitivity and selectivity for chemical analytes. It is widely accepted that the sensitivity of QCM sensors towards a specific analyte is enhanced by increasing the specific surface area of the sensing materials [5]. Recent efforts have been focused on the development of nanostructured coatings on QCM to improve the sensor sensitivity [6,7].

Formaldehyde, one of the most serious indoor air pollutants among volatile organic compounds (VOCs), can cause central nervous system damage, immune system disorders, as well as asthma and nasopharyngeal cancer [8]. The detection of formaldehyde in air is of interest for environmental monitoring and process control since its high toxicity. Feng et al. [9] fabricated a formaldehyde sensor with a detection limit of 28 ppm based on the molecularly imprinted polymers and QCM. The electrospun fibrous membranes with a high specific surface area would be an ideal candidate to replace the flat membrane for further improving the sensitivity of formaldehyde sensors.

Electrospinning is an efficient, relatively simple, and low cost way to produce polymer and composite fibers with diameters ranging from several micrometers down to a few nanometers by applying a high voltage on a polymer solution or melt ejected from a micro-syringe pump [10,11]. These porous three-dimensional (3D) membranes assembled by electrospun fibers are featured with large specific surface area, high porosity, and good interconnectivity [12]. These features of electrospun fibrous membranes provide their potential application in ultrasensitive and highly miniaturized sensors.

Polyelectrolytes have received considerable attention as sensing materials for QCM-based sensors to detect a wide range of chemical analytes [13–16]. Polyethyleneimine (PEI), a cationic

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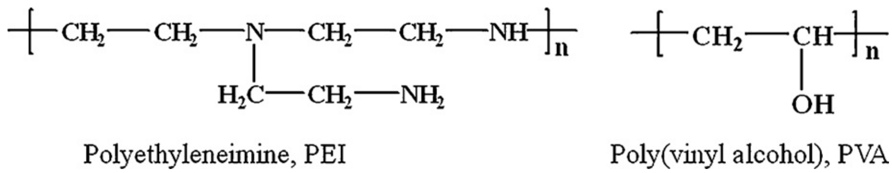

Scheme 1. Chemical structures of PEI and PVA.

polyelectrolyte, has been investigated not only as an immobilization material for biosensors [17,18], but also as a sensing material for various gases and vapors such as H_2S [14], CH_3SH [15], moisture [16], etc. PEI has an affinity with formaldehyde, resulting from the interaction between formaldehyde molecules and amine groups of PEI [19]. Therefore, it can be regarded as an ideal sensing material for the detection of formaldehyde. However, from our pilot study, it is very hard to obtain the pure PEI fibers via electrospinning. Consequently, the water-soluble poly(vinyl alcohol) (PVA) was used as template material [20] to mix with PEI for preparing the sensing fibrous membranes.

In this study, we fabricated a novel formaldehyde sensor based on electrospun fibrous membranes coated QCM and investigated the parameters which affected the performance of resultant sensors.

2. Experimental

2.1. Preparation of polymer solutions

The starting materials included polyethyleneimine (PEI) (M_w 70,000, Alfa Aesar Co., Ltd.) aqueous solution of 30 wt%, poly(vinyl alcohol) (PVA) (M_w 90,000, Wako Pure Chemical Industries, Ltd., Japan), and formaldehyde (GCS grade, Aladdin Chemical Co., China). The chemical structures of PEI and PVA are shown in Scheme 1. Pure water with a resistance of 18.2 MΩ and ethanol (95 wt%, Shanghai Zhenxing Chemical Co., China) were used as solvents.

The 9 wt% PVA solution was prepared from PVA powder and pure water at 80 °C with vigorous stirring. The electrospinning solutions were obtained by blending 0.24, 0.48, and 0.96 g PEI solutions (30 wt%) with 1 g PVA solution (9 wt%) to form the blend solutions with PEI/PVA weight ratios of 0.8/1, 1.6/1, and 3.2/1, respectively. Additionally, in order to know the solvent effect on membrane morphology and sensor sensitivity, 1 g ethanol was added to the mixture of 1 g PVA and 0.48 g PEI solutions with a PEI/PVA weight ratio of 1.6/1.

2.2. Fabrication of fibrous membranes on QCM

Fig. 1 shows the schematic of fibrous membrane deposition on the electrode of QCM via electrospinning. The polymer solutions were placed in a syringe that was connected to the positive electrode of a high voltage power supply (DW-P303-1ACD8, Tianjin Dongwen High Voltage Co., China). Electrospinning of the polymer solutions was conducted at a 2 mL/h feeding rate using a syringe pump (LSP02-1B, Baoding Longer Precision Pump Co., Ltd., China) and a 20 kV applied voltage. The fibrous membranes were deposited on the grounded electrode of QCM (5 MHz, AT-cut quartz crystal with Au electrodes) at a 10 cm tip-to-collector distance. Fibrous membranes were continuously deposited on the electrode of QCM until about 5000 Hz frequency shift was obtained. The resonance frequencies were measured by a QCM digital controller (QCM200, Stanford Research Systems). Fibrous membranes coated QCMs were dried at 25 °C in vacuum for 30 min prior to the subsequent characterizations.

The mass of the membranes deposited on the QCM electrode, as well as the mass of the VOCs adsorbed on the membranes, can be calculated according to the Sauerbrey equation (1):

$$\Delta f = \frac{-2 f_o^2 \Delta m}{A(\mu \rho)^{1/2}} \quad (1)$$

where Δf is the measured frequency shift, f_o is the fundamental frequency of a bare QCM chip (5 MHz), Δm is the mass change per unit area (g/cm^2), A is the electrode area (1.00 cm^2), ρ is the density of quartz (2.648 g/cm^3), and μ is the shear modulus of quartz crystal (2.947×10^{11} dyn/cm^2). As a result, the value of Δf can be converted into the mass loading according to the above-mentioned equation, which means that the frequency is decreased for 1 Hz in the case of 16.67 ng of mass was loaded.

The morphology of fibrous membranes on QCM was examined with field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan). The diameters of fibers were measured using image analyzer (Adobe Photoshop CS2 9.0).

2.3. Preparation of flat membranes on QCM

In order to compare the sensitivity of the fibrous and flat membranes coated QCM sensors, a flat membrane was prepared by casting the blend solution with a PEI/PVA weight ratio of 1.6/1 on the electrode of QCM. The flat membrane coated QCM was dried at 60 °C for 1 h in vacuum. The frequency shift of the flat membrane coated QCM was regulated at about 5000 Hz.

2.4. Apparatus of gas sensing

The experimental setup for measuring the sensing properties of sensors is shown in Fig. 2. The sensor was installed in the testing chamber (9.42 L) which kept with the constant temperature at 22 °C and the relative humidity at 10, 50, 60, and 70%, respectively. A micro-injector (HP5062, Shanghai Eastsen Analytical Instrument Co., Ltd., China) was used for formaldehyde injections. The concentration of injected formaldehyde in the chamber was calculated in

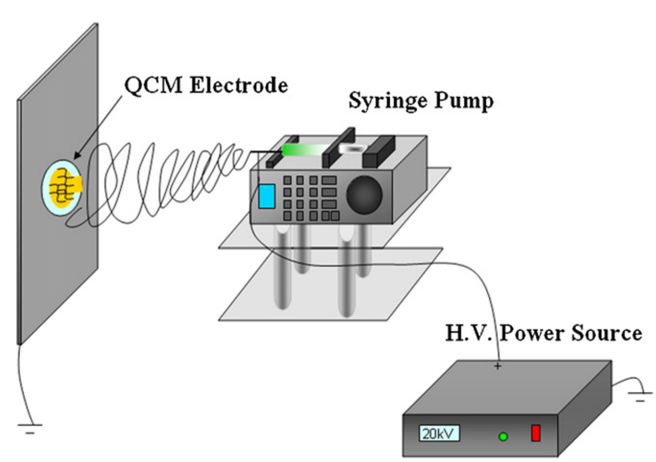

Fig. 1. Schematic diagram illustrating the deposition of fibrous membranes onto the electrode of QCM via electrospinning.