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Functionalized nanoporous TiO_2 fibers on quartz crystal microbalance platform for formaldehyde sensor

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ABSTRACT

This paper describes the detection of formaldehyde through analyses of the resonance frequency signal from quartz crystal microbalance (QCM) sensors coated with a novel organic–inorganic hybrid sensing coating. Nanoporous titanium dioxide (TiO_2) fibers with high Brunauer–Emmett–Teller (BET) surface area (68.72 m^2/g) were fabricated by electrospinning a sol–gel titanium tetraisopropoxide (TIP)/polystyrene (PS) composite solution and following calcination process. Ethylene glycol (EG) dispersed TiO_2 nanofibers were drop casted onto the electrode of QCM, followed by the functionalization of the sensing polyethyleneimine (PEI) on the fibers. The nanoporous TiO_2 fibers covered with PEI layers worked as a highly sensitive sensing interface to provide output signal for weight changes during exposure to formaldehyde vapor. The developed formaldehyde-selective sensors exhibited rapid response and low detection limit (1 ppm) at room temperature. This is because the high specific surface area of the electrospun nanoporous TiO_2 fibers and efficient nucleophilic addition reaction between formaldehyde molecules and primary amine groups of PEI. Our new synthetic methodology promises to be a powerful approach to fabricating hybrid organic–inorganic nanostructures on QCM for gas sensing and chemical analysis.

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1. Introduction

Increasing demands for ever more sensitive vapor sensors for environmental monitoring and control, healthcare, defense and security, and other applications have led to an upsurge of interest in one-dimensional (1D) nanostructures (e.g., nanotubes, nanowires, nanorods, and nanofibers) [1–5]. Recently, 1D nanostructured semiconductor metal oxides (SMOs) based vapor sensors have been demonstrated excellent sensitivity, fast response and recovery [2,6–8]. Particularly, the SMOs nanofibers-based gas sensors prepared by electrospinning technique come into the spotlight [9–11]. These fibrous materials are known for their advances in facilitating rapid mass transfer of the analyte molecules to and from the interaction region and requiring charge carriers to traverse any barriers introduced by molecular recognition events along the entire fiber [12]. Among many available SMOs, due to its chemical stability, high reactivity, non-toxicity and low cost, titanium dioxide (TiO_2) is the most popular candidate used in ultrasensitive sensors, especially in resistive sensors [1,13,14]. For example, Kim et al. [1] have developed an ultrasensitive chemiresistors for the detection of NO_2 based on electrospun TiO_2 nanofiber. The resultant sensor exhibited exceptional sensitivity when exposed to 500 ppb NO_2 at 300 °C. As mentioned above, TiO_2 nanofibers can provide many opportunities for improved sensing behavior of resistive sensors; however, the often-used higher operation temperature restricts their practical use for detecting gaseous pollutants in the environment [12]. Therefore, it is highly desirable to develop a new sensor platform that can be operated at room temperature.

Quartz crystal microbalance (QCM) has been widely used as a room-temperature operated platform for mass sensing by the deposition with the sensitive coatings [15–18]. Their resonance frequency has been proven to decrease linearly upon the additional mass loading of adsorbed associated analytes on the surface of the QCM electrode in a nanogram level [19]. The determination of mass changes is directly related to the interactions between the sensitive coatings and target compounds [16,20]. To date, TiO_2 thin films prepared by liquid phase deposition technique as

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sensing materials on QCM for NH_3 detection have been reported by Georgieva et al. However, the poor specific surface area of such thin film is sometimes a limiting factor to the diffusion of analytes into the sensing materials, and thus leads to less sensitivity (detection limit of 100 ppm) [21]. Electrospun nanofibers with a high specific surface area would be an ideal candidate to replace the flat films to enhance the sensor performances [22,23]. However, on the basis of our current knowledge, no literature about electrospun TiO_2 nanofiber based QCM sensor has ever been reported until now. Additionally, the surface of semiconductor nanofibers can be modified with a monolayer of adsorbed organic molecules [2,24]. Highly efficient dye-sensitized solar cells have been developed by attaching dye molecules to multi-core cable-like TiO_2 nanofibrous membranes [24]. A large surface area of porous TiO_2 fibrous membranes plays an important role in enhancing the light-to-electricity conversion yield of the photovoltaic systems. In this article, we developed a novel nanostructured complex of polyethyleneimine (PEI) functionalized TiO_2 nanofiber (PEI–TiO_2) as sensing coating on QCM for formaldehyde detection. To the best of our knowledge, there have no previous reports of organic–inorganic hybrid porous fibrous membranes composed of SMOs nanofibers covered with polymer layers for use as the sensing coating on QCM for vapor sensing. As-developed QCM sensor showed a good response to formaldehyde vapor at room temperature and it could be used to detect formaldehyde with low detection limit (1 ppm) and good selectivity. Furthermore, another important issue of establishing good adhesion between the SMOs nanofibers and QCM electrodes was also properly addressed to enable practical devices.

2. Experimental

2.1. Materials

The starting materials included polyethyleneimine (PEI) (M_w = 70,000, Alfa Aesar Co., Ltd.), polystyrene (PS) (M_w = 208,000, Wako), titanium tetraisopropoxide (TIP) (Aldrich), formaldehyde (GCS grade, Aladdin Chemical Co., China), pure water with a resistance of 18.2 MΩ, ethanol (Shanghai Zhenxing Chemical Co., Ltd.), ethylene glycol (EG) (Analytical grade, Sinopharm Chemical Reagent Co., Ltd.), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and other volatile organic compounds (VOCs) (Analytical grade, Shanghai Chemical Reagents Co., Ltd.). All chemicals were used as received without any further purification.

2.2. Preparation of TiO_2 nanofibers

TiO_2 nanofibers were prepared by the combination of electrospinning and sol–gel process [25]. In a typical procedure, 1.5 g of TIP was dissolved in the mixture of acetic acid (3 mL) and ethanol (3 mL). After complete dissolution by stirring for 30 min, a 30 wt% PS solution with solvents of THF/DMF (1/4, wt/wt) was added to the solution, followed by magnetic stirring for 1 h. The precursor nanofibers were then electrospun with the electrospinning setup [20]. The precursor solution was delivered to a needle made of stainless steel at a constant flow rate of 4 mL/h controlled by a peristaltic pump (LSP10-1B, Baoding Longer Precision Pump Co., Ltd.), where the metallic needle was connected to a high voltage power supply (DW-P303-1ACD8, Tianjin Dongwen High Voltage Co., China). When a high voltage of 20 kV is applied, fibers were collected on a grounded aluminum foil at an electrode distance of 20 cm. The electrospinning chamber was kept with the temperature of 24 °C and relative humidity (RH) of 40%. The as-spun nanofibers were left in air for 24–48 h to allow the hydrolysis of TIP to go to completion. Finally, TiO_2 nanofibers were obtained by treating them in air at 450 °C for 5 h.

2.3. Preparation of PEI–TiO_2 fibers on QCM

Schematic diagram shown in Fig. 1 presents the fabrication process of sensing PEI–TiO_2 fibers on QCM. A 0.5 wt% TiO_2 suspension was prepared by adding TiO_2 nanofibers into the EG with magnetic stirring for 1 h. In this procedure, EG was used as the dispersing agent due to its lower volatility and higher viscosity than other common organic solvents, which could benefit the dispersion of TiO_2. The TiO_2 fiber EG dispersed phase was drop casted on the grounded electrode of QCM (Stanford Research Systems, Inc.) by a micropipettor (5–50 μL, Shanghai Liansheng Instrumental Factory), followed by heat treatment at 120 °C for 5 h in vacuum until the EG was completely evaporated. The QCM sensors consists of a disk-shaped AT-cut piezoelectronic quartz crystal deposited with gold electrodes on both sides, and are operated at a frequency of 5 MHz. The resonance frequencies were measured by a QCM digital controller (QCM200, Stanford Research Systems). The coating loads of TiO_2 fibers on QCM were regulated at about 1300 and 4000 Hz.

PEI was diluted to 1 wt% with a pure water/ethanol weight ratio of 1:2. The ethanol was used to accelerate the diffusion process of PEI into porous TiO_2 fibers. PEI (1 wt%) solution was drop casted onto TiO_2 fibers by the micropipettor, through which PEI–TiO_2 fibers were prepared. After the solvents completely evaporated at room temperature, the membranes coated on QCM sensors were dried at 25 °C for 12 h in vacuum. The coating loads of PEI on QCM were regulated at about 2700 and 6600 Hz.

2.4. Measurement of sensing properties using QCM technique

The change in resonant frequency of a QCM (Δf) can be related to the change in mass (Δm) due to the adsorption of gas molecules on the surface of the sensing material using the Sauerbrey equation as follows [26]:

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

where Δf the frequency shift (Hz), f_o the fundamental frequency of a bare QCM chip (5 MHz), Δm the mass change per unit area (g/cm^2), A the electrode area (1.00 cm^2), ρ the density of quartz (2.648 g/cm^3), and μ the shear modulus of quartz crystal (2.947×10^{11} dyne/cm^2). As a result, the change of 1 Hz corresponds to the mass of 17.67 ng of materials adsorbed onto the crystal surface of a 5 MHz QCM.

Schematic diagram of a static-type gas testing system is shown as in our previous report [22]. The sensor was installed in the testing chamber (7.64 L) which kept with the constant temperature at 22 °C and the RH of 50%, respectively. A Hamilton microliter syringe (Hamilton Bonaduz AG, Switzerland) was used for analyte injections. The concentration of injected analyte in the chamber was calculated in ppm according to the following equation:

$$C = \frac{22.4\rho T V_s \times 10^3}{273MV} \quad (2)$$

where C the analyte concentration in ppm, ρ_1 the density of liquid analyte in g/mL, T the temperature in testing chamber in Kelvin, V_s the volume of liquid analyte in μL, M the molecular weight of analyte in g/mol, and V the chamber volume in liter. The sensing properties of the sensors to analyte were examined by measuring the resonance frequency shifts of QCM which due to the additional mass loading. The resonance frequencies were measured by the frequency counter. The data from the sensors were recorded by a personal computer.

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