



Cellulose acetate nanofibers coated layer-by-layer with polyethylenimine and graphene oxide on a quartz crystal microbalance for use as a highly sensitive ammonia sensor



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ABSTRACT

A novel approach to the preparation of a sensing coating on a quartz crystal microbalance (QCM) to realize rapid and accurate ammonia detection is reported in this study. Positively charged polyethylenimine (PEI) and negatively charged graphene oxide (GO) were successively assembled on the surfaces of negatively charged electrospun cellulose acetate (CA) nanofibers, using the electrostatic layer-by-layer (LBL) self-assembly technique. Scanning electron microscopy (SEM) images demonstrated the nanofibrous morphology of the as-prepared CA/PEI/GO membrane. Fourier-transform infrared (FT-IR) and Raman analyses indicated that the PEI and GO were successfully assembled on the surfaces of the CA nanofibers. In gas-sensing tests, the CA/PEI/GO-based QCM sensor not only exhibited a low detection limit and rapid response, but also performed with good reversibility and selectivity with respect to ammonia detection.

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1. Introduction

Ammonia is an important raw material, widely used in chemical processes, fertilizers, food processing, and medical diagnosis, among others, but it is also a hazardous alkaline gaseous pollutant that contributes to eutrophication, impacts health, and promotes climate change [1,2]. In particular, the long-term exposure to ammonia through the skin, eyes, throat, or lungs can harm human health, leading to many disease states, including severe skin and ocular irritation, respiratory disorders, nausea, headache, and even death [3,4]. At concentrations over 55 ppm, ammonia can be easily identified by our natural sense of smell [5], but we fail to detect it in lower amounts and are unable to quantify exact ammonia concentrations. However, because of its toxicity, the monitoring of ammonia is required and regulated in many fields [6]. Short term (15 min) and long term (8 h) occupational exposure limits have been established at 35 and 25 ppm by the US Occupational Safety and Health Administration (OSHA), respectively [7]. In the automotive industry, the indoor detection limit has been set near the olfactory limit of ~50 ppm [8]. Near intensive farming areas,

the ambient ammonia concentration limit is set at 25 ppm [9]. The chemical industry has set 20 ppm as the upper limit for a dangerous ammonia concentration [10], and the limit in the breath analyses used in medical settings is as low as 2 ppm [11].

Because of its toxicity and potential threats to human health, there is an increasing need to develop effective methods suitable for monitoring low levels of ammonia in diverse fields. To date, sensors based on various sensing techniques, including impedance [12,13], mass [14], and optics [15,16], have been investigated. Among these sensors, most optical sensors are complex, expensive, and require much miniaturization and integration. Electrical sensors usually have low gas selectivity in a mixed gas environment. However, as mass-sensitive detectors, quartz crystal microbalance (QCM)-based sensors have frequently been proposed for the fabrication of rapidly responding and highly sensitive and selective gas sensors [17–19]. Moreover, QCMs are inexpensive, relatively easy to use, more stable during long-term operation, and have high potential for integration.

It is widely accepted that the sensing characteristics of QCM sensors can be enhanced by applying nanostructured materials such as nanowires [20], nanotubes [21], nanoparticles [22], and nanofibers [23], to take advantage of their large specific surface areas (SSA). Compared with other methods, electrospinning is widely regarded as an effective, facile, and low cost approach for the manufacture of nanofibers under high electrostatic voltages [24–26]. Electro-

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spun nanofibers can be tailored in terms of diameter or structure to obtain the unique characteristics of ultra-thin fibers, high SSA, and three-dimensional (3D) structures, which makes them promising in the fabrication of ultrasensitive sensors [27–29]. In 2004, Ding et al. first introduced electrospun nanofiber/QCM gas sensors for ammonia detection [30]. To improve the sensitivity of these sensors, Wang et al. developed two-dimensional nano-nets comprising interlinked ultrathin nanowires with diameters of 10–30 nm [31]. These unique ultrafine fibers had relatively high surface areas, and the related electrospun nano-net/QCM sensors exhibited low detection limits, as well as quick response and good selectivity for gas detection. Therefore, the sensitivity of a sensor mainly depends on the surface area of the sensing materials.

Recently, graphene and chemically modified graphene have aroused considerable research interest owing to their advantageous mechanical, thermal, and electrical properties. As a consequence of their unique structure that consists of two-dimensional monolayers of atomic carbon, all of the carbon atoms or sensitive groups would be exposed to an analyte. This remarkable property makes them a promising option for use as ultrasensitive gas sensors. X. Y. Li et al. [32] constructed a QCM ammonia sensor that utilized graphene oxide (GO) as an isolation layer between the electrode of the QCM and a polyaniline (PANI) film. Compared to the properties of the QCM with pure PANI, the ammonia sensitivity of GO-modified QCM was effectively improved, affording a detection range from 100 to 1600 ppm. In our previous work [33], GO was added into polystyrene solution to fabricate composite nanofibers via electrospinning. These fibers comprising ultrathin nanowires presented a large surface-active region, and good sensing behaviors including a low detection limit of 1 ppm and good reversibility for ammonia detection when combined with a QCM sensor system. However, the poor dispersion of the GO in the spinning solution restricted its sensitivity in sensor applications. The response value (frequency shift) was as low as 0.3 Hz when exposed to ammonia at a concentration of 1 ppm.

These results for the composite electrospun nanofibers spurred our interest in improving the dispersibility of GO and expanding the selection of potential sensing materials that can be incorporated into electrospun nanofiber/QCM systems. Therefore, in this study, an electrostatic layer-by-layer (LBL) self-assembly technique was utilized to fabricate sensing coatings on QCMs [34,35]. Positively charged PEI and negatively charged GO layers were successively assembled on the surfaces of negatively charged cellulose acetate (CA) nanofibers electrospun on the QCM electrode. The sensor fabricated with the LBL technique had a high electrospun-membrane SSA, along with an optimal surface morphology as regards exposure of the sensing material to the analyte, which led to excellent sensing performance for ammonia. To the best of our knowledge, this is the first study of a QCM sensor fabricated using electrospun CA nanofibers coated with PEI and GO as sensing materials.

2. Experimental

2.1. Materials

The starting materials CA (100 kDa, J&K Scientific Ltd., USA), liner PEI (70 kDa, 50 wt% aqueous solution, Aladdin Chemical Reagent Co., China), GO aqueous suspension (2 mg/mL, GO sheets diameter: 50–200 nm, surface oxygen content: 35.8%, Nanjing XFNANO Materials Tech Co. Ltd., China), analytical grade acetone, ethanol, dichloromethane, formaldehyde, tetrahydrofuran and *N,N*-dimethylacetamide (DMAc). Ammonia (analytical grade, degree of purity: 99.999%) and the interfering gases (NO, NO₂, H₂S, and SO₂, degrees of purity: 99.9%), were supplied by Gaonengda Chemical Industry Co. Ltd. (Zhaoqing, China).

2.2. Fabrication of nanofibrous CA mats on QCM

Fig. 1a schematically presents the fabrication and deposition of the nanofibrous CA mats on the QCM. A 15 wt% CA solution was prepared by adding CA to a mixed solvent (2:1 acetone:DMAc, w/w) under moderate agitation for 6 h at room temperature. The solution was loaded into a syringe that was then connected to a high-voltage power supply (Dalian Teslaman High Voltage Co. Ltd., China). During electrospinning, a solution feed rate of 1 mL/h was maintained using a peristaltic pump (LSP01-2A, Baoding Longer Precision Pump Co. Ltd.). The temperature and relative humidity (RH) of the electrospinning environment were maintained at 25 °C and 55%, respectively. Keeping the voltage at 15 kV and the distance between the pinhead and QCM golden electrode (Mark frequency: 5.0 MHz, Diameter: 25.42 ± 0.03 mm, AC5AD25, JJK Electronic Co., Ltd.) at 15 cm, the CA nanofibers were continuously deposited on the grounded electrode of the QCM for 5 s, and then dried under vacuum at 80 °C for 3 h to remove the excess solvent. The frequency of blank QCM electrode was considered as starting point, and the frequency shift of the CA nanofibers tested later was approximately 1000 Hz.

2.3. Fabrication of LBL films on nanofibers

The LBL deposition process was used to distribute the PEI and GO on the nanofibrous CA membranes. First, the CA-membrane-coated QCMs were immersed into a 10⁻³ M (based on the repeat unit, 70 g/L) PEI solution for 20 min, followed by 2 min of rinsing in four pure water baths, and subsequent drying at 80 °C for 2 h under vacuum to remove the solvent. The frequency shift of the CA/PEI-coated membrane was approximately 1200 Hz. The prepared PEI-modified CA membranes (CA/PEI) were then immersed into the GO solution for 20 min, followed by identical rinsing and drying steps as above. The prepared QCM-sensors were then ready for characterization and performance evaluation, the frequency shift of CA/PEI/GO-coated membrane was around 1500 Hz.

2.4. Sensor apparatus for ammonia detection

A schematic diagram of the ammonia-sensing system is presented in Fig. 1b. The QCM sensor was installed in a test chamber (10 L) in which the operating temperature and RH were monitored in real time using a thermohygrometer (Testo 605-H1, Testo Ltd., Germany). High purity ammonia gas or other interfering gas was injected into the chamber using a modified gas-injection system according to Qu's work [36], and the flow rates of ammonia were maintained by mass gas flow controllers (MCS-Series, Alicat Scientific Inc., USA). The ammonia-sensing performance of the QCM sensor was determined by monitoring the shift in resonance frequency, which varies in response to the additional mass loading of the adsorbed ammonia molecules on the QCM. The resonance frequencies were measured using a QCM digital controller (QCM-1000, Nanosensing Research System), and the sensor output data were recorded on a computer. The mass of the absorbed ammonia (Δm) was calculated using the Sauerbrey equation, as follows [37]:

$$\Delta f = -2f_0 \cdot f_n \Delta m / A(\mu\rho)^{1/2} \quad (1)$$

where Δf represents the frequency shift of the QCM sensor (Hz); f_0 is the intrinsic frequency of an empty QCM platform; f_n is the resonant frequency of the overtone ($f_n = n \cdot f_0$, $n=3$ in this study); Δm is the mass variation per unit area (g cm⁻²); A is the electrode surface area of the QCM (1 cm²); and μ and ρ are the shear modulus and density of a quartz crystal, 2.947 × 10¹¹ dyne cm⁻² and 2.648 g cm⁻³, respectively. In this study, the inherent frequency of

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