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Short Communication

Phenylacetic acid-modified nanofibrous polystyrene membranes for use as highly sensitive ammonia sensors

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ABSTRACT

Phenylacetic acid (PA) was selected as the sensing material for the detection of ammonia in gas sensor fabricated by coating PA modified polystyrene (PS) nanofibrous membranes on a quartz crystal microbalance (QCM) electrode. These membranes were assembled with wrinkled-surface electrospun nanofibers to create a three-dimensional (3D) structure with a large specific surface area of 45.81 m^2/g. Through FE-SEM imaging, it was revealed that the morphology of the fibers was barely altered after the modification procedure, with FT-IR and DSC analyses confirming that the PA was dispersed on the substrate. This sensor structure exhibited a rapid response combined with a low ammonia detection limit (1.5 ppm).

1. Introduction

Ammonia is well known to be capable of causing skin irritation, respiratory disorders and nausea, with the maximum allowable concentration limit in air being 50 ppm for indoor situations, but a much stricter 20 ppm in the workplace [1]. Breath analysis in medical applications, however, requires a low-cost and fast ammonia gas sensor that can detect levels of less than 2 ppm [2].

There have been various sensors developed to detect ammonia, including resistance sensors, amperometric sensors, photoelectric sensors and acoustic wave sensors [1]; moreover, quartz crystal microbalance (QCM) technique has also been widely used over recent years for determining low gas concentrations because of its high sensitivity, fast response and durability [3]. These properties of QCM can be further enhanced when combined with electrospun nanofibers. For instance, Ding et al. have achieved a high sensitive sensor by depositing electrospun polymer nanocomposites on a QCM electrode [4], and Zhang et al. developed it by coating sensing polymer modified nanofibrous membranes on the electrode [5].

Different from previous approaches, this study employed the small molecule phenylacetic acid (PA) as the sensing material, with the aim of using its good fluidity to ensure its uniform dispersion on the surface of the nanofibers. This was used as the basis for fabricating a unique sensor structure through the deposition of PS nanofibers onto QCM via electrospinning, followed by PA modification of the PS nanofibrous membranes. The morphology, structure and chemical composition of this sensor were herein investigated, as well as its sensitivity to ammonia.

2. Experimental

2.1. Materials

Polystyrene (PS) (350 kDa) and phenylacetic acid (PA) were obtained from Aldrich. N,N-Dimethylformamide (DMF), ethanol and dichloromethane were purchased from Sinopharm Chemical Regent Corporation in Shanghai, China.

2.2. Fabrication of sensing materials on QCM electrode

Fig. 1a briefly depicts the procedure used to fabricate the sensing materials. In this, a 10 wt% PS solution in DMF was pumped by a peristaltic pump through a 5 mL syringe connected to the positive electrode of a high voltage power supply. Using a 1 mL/h feeding rate, 25 kV applied voltage and a constant environment of 25 °C and 50% humidity, fibers were continuously deposited onto a grounded QCM electrode at a tip-to-collector distance of 19 cm. The frequency shift of the electrospun membrane over 15 s was approximately 1000 Hz. The resulting membrane-coated QCM sensors were dried for 1 h at 70 °C in vacuum, after which 5 μL of a 5 wt% PA solution in ethanol was deposited and dried for 1 h at 30 °C in vacuum to remove ethanol.

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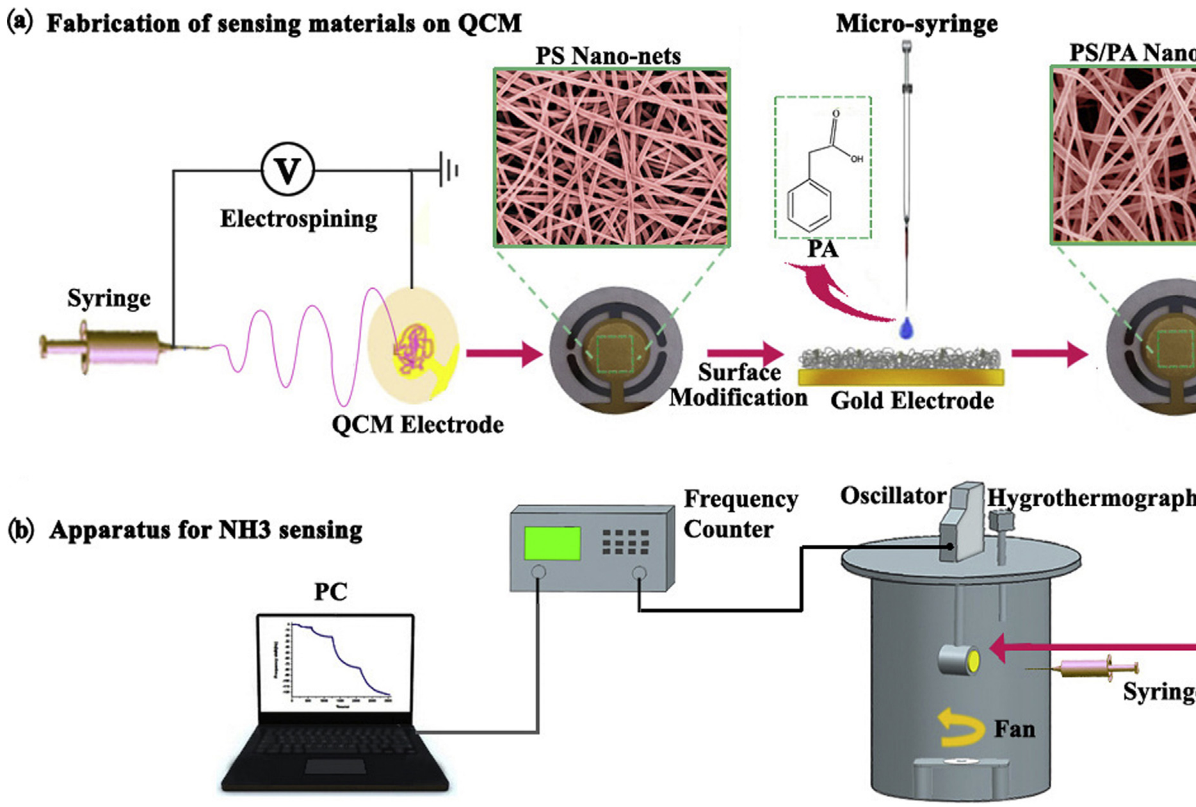

Fig. 1. Schematic of the fabrication of sensing membranes on QCM (a) and the ammonia testing system (b).

2.3. Apparatus for ammonia sensing

The experimental setup used for measuring ammonia is shown in Fig. 1b, where it could be seen that the sensor was installed in a 10 L testing chamber. The RH and temperature in the chamber were monitored in real-time using a thermo-hygrometer. Once this setup had stabilized, various concentrations (1.5, 5, 10, 25 and 50 ppm) of ammonia were injected into the chamber. The resonance frequencies were then measured via a QCM digital controller and the frequency shifts were recorded by a computer.

2.4. Characterization

The morphology of the membranes was characterized by field emission scanning electron microscopy (S-4800, Hitachi Ltd., Japan); the diameters of the fibers were measured by an image

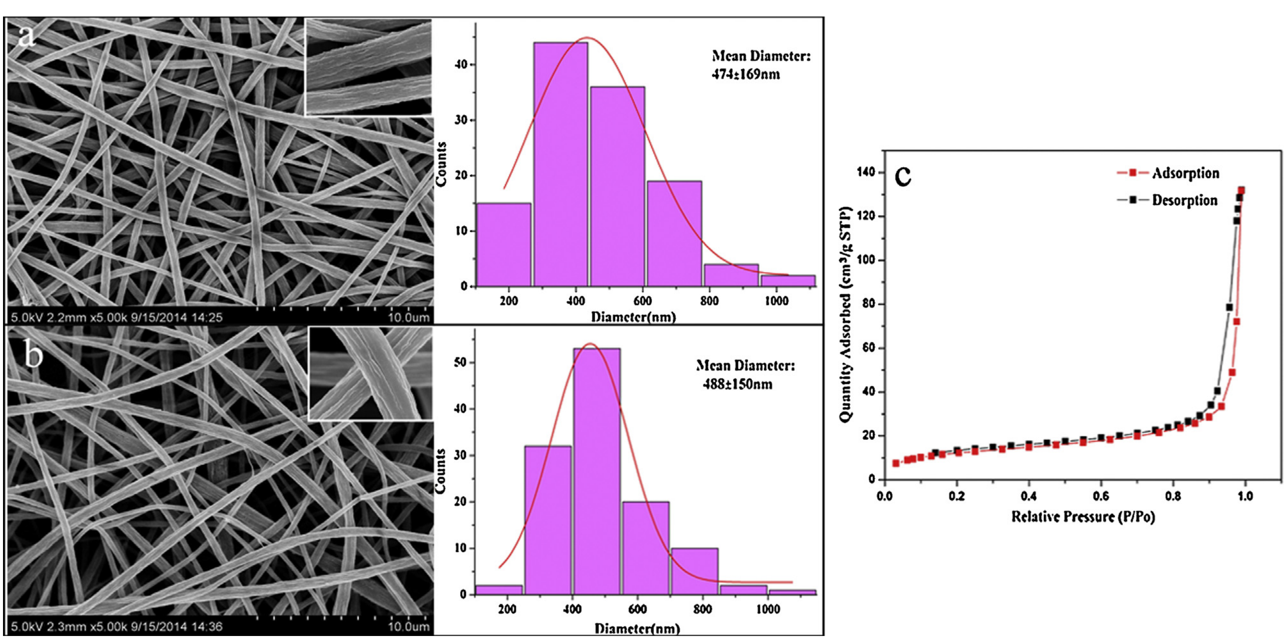

Fig. 2. FE-SEM images of pure PS membrane (a) and modified PS membrane (b); specific surface area of PS membrane (c).