Fabrication of textile based conductometric polyaniline gas sensor

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ABSTRACT

In this work, we report the fabrication of gas sensors prepared by in situ polymerization of aniline on non-woven fabrics. It is anticipated that a thin coating of polyaniline film fabricated on porous fabric material would improve the performance of the polyaniline based gas sensor. The hypothesis is based on the recent improved technique that allows the fabrication of nanoparticle based polyaniline film, and the high gas permeability of the fabrics. Sensor fabrication parameters which included acidity of reaction media, precursor and reagent concentrations, and the number of modification cycle have been studied. The resulting gas sensors were found to be highly responsive to a range of volatile organic compounds (VOCs). This high sensitivity was also accompanied with fast response time ($\sim$10 s). The order of sensitivity to VOCs was found to be ethanol > chloroform > toluene > acetone > ethyl acetate. Further, the sensor was three orders of magnitude more sensitive to ammonia than all organic vapours tested.

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1. Introduction

Simple, low cost and energy efficient gas sensors for VOCs measurements are in great demand for applications in industries and for environmental analysis. There are many gas sensing devices available commercially at present, covering very large and diverse area of applications [1–6]. Most common sensors include tin oxide gas sensors [6,7], electrochemical (amperometric and conductometric) sensors [7,8,5,9], colorimetric sensor [10–12] and optical sensors [11–14]. Despite of the good analytical performance of these sensors they are generally expensive, power hungry and require constant maintenance which can also be costly. In light of these, much research has been focused on the development of robust gas sensing material with simple transduction principle which could lead to sensing devices with low operation cost. Among these are the investigation of using inherently conducting polymers such as polypyrole, polythiophene and polyaniline (Pani) for gas sensing [15–19]. Advantages of using conducting polymers as sensing materials are that they are reversible, light weight, flexible, low cost and require simple fabrication processes [16]. Pure polymer films, polymer blends and polymer–inorganic composites have been studied [19–24].

Generally, pure conducting polymer film based gas sensors are fabricated on solid electrode substrates such as thermal plastics (PMMA), ceramic or silicon. Good sensitivity and fast responding sensors have been reported [16–19]. Other attempts to improve the sensor performance include using metal, metal oxide and non-metallic oxides to form conducting polymer composites that make use of the catalytic effect of the metal or metal oxide. Selectivity of the Pani based gas sensors have been reported to have improved markedly [5,9,19–21]. Other methods include modifying the surface morphology of Pani film to improve gas permeability in order to enhance the sensitivity and respond time [21–25].

Our previous research has shown that the surface morphology of Pani film can be controlled by reaction parameters to achieve surface with nano or micro features; and these surface features have been shown to affect sensor sensitivity [26–28]. This paper reports our attempt in improving the performance of Pani based gas sensor by in situ fabrication of Pani coating onto a porous non-woven fabrics. Optimization of reaction conditions for the textile modification and the resulting sensor performance are presented.

2. Experimental

2.1. Materials

Ammonium persulfate (APS, CAS: 7727-54-0, analytical grade reagent), sulfuric acid (98%) and all the VOCs used were all analytical grade reagents from Sinopharm Chemical Reagent Co. Ltd. (China) and were used as received. Aniline (CAS: 62-53-3,

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analytical grade reagent) was distilled under reduced pressure before use. The non-woven fabrics made from polypropylene fibres used for preparing gas sensors were obtained from retail shops and was pre-washed with deionized water before use.

2.2. Fabrication of conducting polymer based gas sensor

2.2.1. General procedure for sensor fabrication

Typical sensor fabrication procedure is described as follow: The non-woven fabric was cut into small sample size of 5 cm width × 5 cm length. Individual fabric samples were pre-soaked in a 20 mL mixture containing 0.2 M aniline and 0.2 M H_2SO_4 for 10 min at room temperature before polymerization. Then the sample was removed from the preconditioning vessel, and excess water was shaken off from the fabric surface before it was transferred into a polymerization vessel containing 20 mL of 0.1 M APS for a desired period of time to allow the polymerization reaction to proceed. The sample was then removed from the reaction vessel and thoroughly rinsed with deionized water. This cycle of pre-soaking and poly-merization was performed several times to afford different PANI coating thicknesses. A visual colour change from white to pale green to dark green was observed with increasing number of surface mod-ification cycle. The coated fabric samples were dried under vacuum for 24 h in a vacuum drying oven (Shanghai Boxun Apparatus Co. Ltd., DZF-6020, China) at 70 °C before sensor characterization.

2.2.2. Optimization of sensor fabrication technique

Different parameters including reagent concentration, reaction time, order of fabrication procedure and number of fabrication cycle for preparing the textile sensor were investigated. Fabrica-tion methods 1–4 investigate different order of reagent uptake by the fabric in relation to the resulting surface morphology. Sensor samples prepared from various fabrication procedures FP1 to FP4 described below are referred to as S1 to S4 respectively.

Reagents: (i) 0.2 M aniline in 0.2 M H_2SO_4, (ii) 0.1 M APS in H_2O, (iii) 0.1 M APS in 0.2 M H_2SO_4.

FP1: Fabric sample was pre-soak in a 20 mL of (i) for 10 min; then fabric was transferred into a polymerization vessel containing 20 mL of (ii) for 5 min. Different number of fabrication cycle was also investigated.

FP2: Fabric sample was pre-soak in a 20 mL (i) for 10 min, then transfer the fabric into a polymerization vessel containing 20 mL of (iii) for 5 min.

FP3: Fabric sample was pre-soak in a 20 mL of (ii) for a 5 min, then transfer the fabric into a polymerization vessel containing 20 mL (i) for 10 min.

FP4: Fabric sample was immersed in 20 mL of (i) at 0 °C controlled by ice water mixture, then 20 mL (ii) was add into the vessel at the rate of two drop per second. The reaction was allowed to proceed for 2 h.

Results suggested that FP1 was the preferred order of reagent mixing; variation of reagent concentration used in FP1 was then investigated.

Optimization of FP 1

(a) Varying acidity: 0.2 M aniline solutions were made up in 0.1 M, 0.15 M, 0.2 M, 0.5 M, 1.0 M and 1.5 M H_2SO_4.
(b) Varying aniline concentration: aniline concentrations of 0.1 M, 0.15 M, 0.2 M, 0.25 M, 0.3 M, 0.4 M and 0.5 M were studied.
(c) Varying oxidant concentration: APS concentration of 0.02 M, 0.05 M, 0.1 M, 0.2 M, and 0.25 M were used.

2.3. Measurement procedure

A PANI coated fabric of 2 cm × 3 cm ($W \times L$) was used as sen-sor for volatile organic compounds analysis. Conductive copper adhesive tape was fixed onto either sides of the fabric sensor as electrical contacts. The sensing chamber was constructed as follow. The sensor was fixed under the rubber cap of a glass container by two crocodile clips attached to electrical wires that penetrated through the rubber cap. Several identical containers were flushed with nitrogen first, then a fixed volume of different VOC samples was injected into each container followed by sealing with a lid to allow sample to reach equilibrium for at least 30 min. To measure sensor response to saturated VOC vapour, the lid of the sample con-tainer was replaced by the rubber cap with the sensor attached. The responses (change in electrical resistance) of the PANI fabric sensor was measured with two probes method using a UT70d Multimeter (Shanghai, China) connected to a PC via RS232 connection. During measurement, the sensor was exposed to the saturated headspace of the VOCs at room temperature of around 25 °C until sensor response reached equilibrium. Then the sensor was removed and allowed to recover in an empty container prefilled with nitrogen.

To measure sensor response to different concentrations of indi-vidual VOCs, a single container fitted with the sensor cap was used. The container was first flushed with nitrogen from a balloon to clean out residue vapour from previous experiment, then clean air was reintroduced before measurement. When a stable baseline (R_0) was established, a fixed volume of a VOC sample was injected through the rubber cap using a precision micro syringe. A home-made magnetic stirrer fan was used inside the chamber to aid the dispersion of the VOC; typically it took around 30 s for low boiling liquids, such as ethanol and chloroform, to completely vaporize at room temperature (around 25 °C). When the sensor response had reached equilibrium, subsequent injections were made in a similar fashion.

The data were logged and stored in the PC directly before processing using Microsoft Excel™. A normalized sensor responses S, where

$$S \ (\%) = \frac{R - R_0}{R_0} \times 100 \tag{1}$$

was used for data analysis; where R is the sensor response to the analyte and R_0 is the baseline resistance.

The vapour concentration during calibration was calculated according to the equation:

$$c_{ppm} = \frac{V_G \times \rho}{M} \times \frac{T}{273} \times 22.4/V_D \times 10^6 \tag{2}$$

V_G is the volume of solvent injected; ρ is the density of vapour; M is the molecular weight; T is the temperature; V_D is the volume of test chamber.

3. Result and discussion

3.1. Progress of PANI growth on non-woven fabrics

A detail investigation of the growth of Pani on non-woven fab-ric with respect to fabrication cycle was carried out using the procedure described in FP1. Results have shown that the initial deposition of Pani on the bare fabric was quite slow. It seems that a 'priming stage' was required during which nucleation occurred on the bare fabric surface as shown in Fig. 1, SEM images C1, where small amount of Pani clusters were observed to scatter on the fab-ric surface after the first fabrication cycle. The image C2 (sample after the second cycle) does not show increase population of Pani clusters because a 'clean area' was selected to be viewed to show the surface ripples. After the third cycle, most of the surface had