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Research Paper

Facile fabrication of flexible SiO_2/PANI nanofibers for ammonia gas sensing at room temperature

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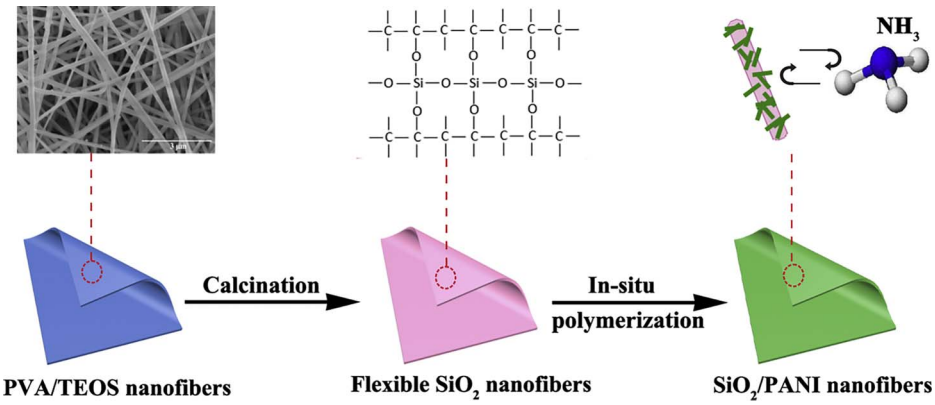
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, we report a novel ammonia (NH_3) sensor material with outstanding sensing performance based on free-standing polyaniline (PANI) coated inorganic silica (SiO_2) nanofibers (SNF) membranes, which could work well at room temperature. SNF membranes were prepared by the combination of sol-gel, electrospinning and calcination methods It was realized per the results that the flexibility of SNF membranes could be considerably controlled by calcination temperature. SNF were diverted from flexible to brittle as the temperature increased from 600 °C to 1000 °C. In order to adapt to wearable gas senor demands, flexible SNF membranes obtained from heat-treated at 600 °C and 800 °C were used as templates for in-situ polymerization of aniline. The gas sensing behavior of PANI coated SNF of 10 ppm to 300 ppm NH_3 were operated at room temperature. Gas sensing tests revealed that the SNF/PANI composite nanofibers had high response values. Additionally, the gas sensing abilities of PANI coated on SNF annealed at 800 °C was much higher than SNF treated at 600 °C. Moreover, the PANI coated SNF (annealed at 800 °C) could detect NH_3 to 400 ppb, as well as showed excellent selectivity, repeatability and reversibility. The flexible SNF/PANI membranes were easy to prepare and it obtained ideal flexibility, which exhibited their potential for applying as wearable gas senor.

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1. Introduction

NH_3 is generally present in chemical, food, biomedical and environmental conservation activities. It is colorless, pungent with high toxicity and severely irritating [1–4]. It is known by fact that even a smaller amount of NH_3, over 35 ppm in environmental air, could damage human health within 15 min [5]. Inhalation of NH_3 may cause acute respiratory disease, such as laryngitis, tracheobronchitis, bronchopneumonia and even pulmonaryedema. Therefore, due to the extensive sources and great harm of NH_3, it is crucial to exploit a NH_3 sensor with high sensitivity and great efficiency for health care, environmental protection and industry safety. Conducting polymers on the other hand have been increasingly used as efficient medium for chemical sensing, based on electronic transfer arising between the polymeric films and gas molecule as the gas vapor adsorption occurs [6]. Compared with metal oxide materials which always operate at high temperature [7–10], conducting polymers could circumvent the limitation that they can operate at room temperature. PANI is one of the most frequently used materials for sensing due to its facile synthesis, high conductivity, unique doping/dedoping chemistry reaction and high responsibility to NH_3. Kumar. et al. [11] designed a flexible PANI film NH_3 sensor, in which PANI was deposited on polyethylene terephthalate (PET) films by in-situ polymerization with aniline monomers. The results exhibited a higher response, reproducibility, stability with low measured limitation ($\sim$5 ppm). Uh. et al. [12] fabricated 1D PANI nanofibers via electrospinning process with hydrochloric acid, which was successfully used to detect NH_3 with a limit of 10 ppm. Vaghela. et al. [13] prepared a kind of agarose–guar gum-polyaniline (A–G-PANI) composite films which marked NH_3 sensing behavior within the range of 10–90000 ppm.

It is notable that the structure of gas sensor material has big impact on gas sensing properties. Among the huge number of gas sensing materials, nanofibers have demonstrated several remarkable characteristics such as high specific surface area, high porosity and small size [14,15]. Electrospinning is a versatile, efficient and easy-to-handle method for fabricating nanoscale polymer or composite fibers through the application of high voltage on a viscous polymer solution or melt [16–18]. Electrospun nanofibrous membranes can be applied in many fields, such as tissue engineering [19], solar cells [20] and catalysts [21], lithium-ion batteries [22], et al. They are also ideal candidates for sensors [23–25], by virtue of the porous structure that could accelerate the gas diffusion. In addition, the fibrous reticular structure prompts the transportation of charge [26–28] and apparently providing more electrochemical reaction sites and adsorption area. Flexible gas sensing materials have attracted a great deal of attention in the development of wearable and portable handheld sensors. Nanofibrous SiO_2 is considered as an outstanding base material due to its adsorption of reaction, chemical inertia as well as high specific surface area and good recyclability [29,30]. Frangibility has limited the application of conventional ceramic fibers. The combination of sol-gel process and electrospinning with subsequent pyrolysis has been proven as an effective method to synthesis flexible SiO_2 nanofibers [31–33]. SiO_2 nanofibers membranes have been used for high-heat-resistant materials, filtration materials and dye-sensitized solar cells et al. [34], but the development of flexible SiO_2 nanofibrous membranes for gas sensing domain was seldom reported.

In this work, we fabricated flexible inorganic SNF membranes by the combination of sol-gel method, electrospinning technique and calcination process. Our results revealed a direct relation between the diameter and crystalline phase of these nanofibers and varied calcination temperatures, resulting in flexibility transformation of the SNF membranes. The flexible SNF/PANI gas sensors were prepared via in-situ polymerization with aniline monomers, which owned ideal nanofibrous structure that could enhance the response capabilities. The mechanism of flexible structure formation and NH_3 sensing were discussed in details.

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA, M_w = 22000) was purchased from Vita Chemical Co., Shanghai, China. Tetraethyl orthosilicate (TEOS) was obtained from Bo Di Industrial Co.Ltd.,Tianjin, China whiles oxalic acid ($C_2H_2O_4$), aniline monomer (An), ammonium persulfate (APS) and hydrochloric acid (of concentration was 37%) were purchased from Sinopharm Chemical Reagent Co.Ltd. (Shanghai, China). Aniline monomer was used after distillation, and the rest of chemicals and reagents were used as received. Deionized water was used in this study.

2.2. Preparation of precursor solutions

25 wt% PVA solution was prepared by dissolving PVA in deionized water at 80 °C under stirring for 4 h. TEOS, H_2O and $C_2H_2O_4$ with the molar composition 1:8.1:0.19 was added into deionized water with stirring at room temperature for 7 h to prepare silica gel. Then 10 g PVA solution was dropped slowly into 20 g silica gel followed by stirring for 7 h. Thus, the precursor solution for electrospinning was obtained.

2.3. Fabrication of flexible silica membranes

Firstly, the precursor solution was placed in a 20 mL syring with a feed rate of 1 mL h^{-1} whereas a grounded drum covered with aluminum foil was used as the collector. Applied DC (direct current) voltage was 20 kV, and the selected tip-to-collector distance was 18 cm. To fabricate silica flexible mats, the composite PVA/silica fibrous membranes were calcined from room temperature to 600 °C, 800 °C and 1000 °C respectively at 5 °C $min^{-1}$and kept for 3 h in air atmosphere. The fibrous mats obtained from PVA/silica mats were denoted as SNF1, SNF2 and SNF3.

2.4. Preparation of SNF/PANI gas sensor

SNF membranes were immersed in a solution of aniline and 1.2 mol/L HCl mixed solution for 3 h after which 30 mL 1.2 mol/L HCl solution containing APS was slowly dropped in the mentioned solution for in-situ polymerization. The mole ratio of aniline to APS was 1:1. The polymerization was implemented in an ice water bath at 0–5 °C for 5 h. The SNF/PANI were washed with deionized water and HCl solution and then dried in vacuum at 50 °C for 24 h. Fig. 1 shows the schematic of the fabrication of SNF/PANI. The SNF/PANI membranes were cut into small patches (5 mm × 8 mm). The cut mats were stuck on the test benches by the silver paste and allowed to dry. Schematic illustration of the assembled testing element is shown in Fig.S1. Correspondingly, the three gas sensors are named as SNF/PANI-1 sensor, SNF/PANI-2 sensor and SNF/PANI-3 sensor.

2.5. Characterization

The crystalline structure of SNF membranes were examined by an X-ray diffraction instrument (XRD, D8, Bruker AXS, Germany). The morphologies and structures of the PVA/SiO_2 membrane, SNF membranes, SNF/PANI hybrid membranes were characterized by a field emission scanning electron microscope (FESEM, SU-1510, Hitachi, Tokyo, Japan), transmission electron microscope (TEM, JEM-2100HR, JEOL), and Fourier transform infrared (FTIR) spectra in a range of 4000–400 cm^{-1} with a 4 cm^{-1} spectral resolution by using a NEXUS 470 spectrometer (Nicolet, Madison, WI, USA). TG and DTG were performed by an STA 499 F3 thermo-analyzer (Netzsch, Germany) in air from 30 °C to 1000 °C.