Nanostructured polyaniline/poly(styrene-butadiene-styrene) composite fiber for use as highly sensitive and flexible ammonia sensor

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ABSTRACT

Sensors with flexible and stretchable features are of great interest owing to their potential applications in flexible electronics. To this date, to fabricate gas sensors with both high sensitivity and flexibility is still a challenge. Herein, we have successfully coated thin film of polyaniline (PANI) onto flexible poly(styrene-butadiene-styrene) (SBS) fiber using in-situ dilute polymerization. The SBS/PANI composite fibers were evaluated as ammonia gas sensor. Morphological analysis of the nano-composite fiber revealed that the thin film consists of interconnected PANI nanofibers. Due to the high surface areas of the interconnected PANI nanofibers and the super flexibility of SBS fiber substrates, the SBS/PANI composite fiber based sensor demonstrated fascinating performance, including superior sensitivity (5.8 for 25 ppm, 16.4 for 100 ppm), fast response (≤ 13 s), good reproducibility as well as excellent mechanical reliability. Notably, the gas sensor is capable of sensing a concentration of ammonia gas as low as 0.1 ppm at room temperature. Based on its superior performance, its application in detecting ammonia gas leak is demonstrated, signifying its tremendous potential for applications in flexible electronics.

1. Introduction

Ammonia is well recognized as hazardous industrial gas, which can cause serious problems to both environment and public health even at very low concentration [1,2]. Therefore, the detection of ammonia is an urgent need for numerous applications, including environmental monitoring [3,4], food industries [5,6], and more recently in biomedical diagnosis [7,8]. So far, numerous ammonia sensors have been developed, based on inorganic metal oxides [9], hybrid materials [10–12], and conducting polymers [13,14]. Among which, conducting polymers may be a potential alternative owing to some advantages such as ease of synthesis, processing, modifiable electrical conductivity, and operability at room temperature [15–17]. In particular polyaniline (PANI) has been extensively studied as an efficient ammonia gas sensing material due to its unique doping/dedoping chemistry, stable electrical conduction and good environmental stability [18–21].

One-dimensional (1D) nanostructured forms of PANI, such as nanofibers and nanorods have gained exceptional attention due to their high surface area and porosity which allows for rapid diffusion of analytes into and out of the structures [22]. For example, Virji et al. [23] employed interfacial polymerization method to synthesize PANI

nanofibers which exhibited significantly much better performance than conventional PANI films in both response sensitivity and rate. Rutledge et al. [24] also electrospun PANI nanofibers for chemiresistive gas sensors. The fibers showed excellent sensing performance to ammonia and nitrogen dioxide due to their ultra-high specific surface areas. Although the use of PANI nanofibers offers the prospect of high sensitivity and rapid response, the application of PANI nanofibers is limited by their poor mechanical strength and flexibility resulting partly from their rigid conjugated backbone structure and the fabrication techniques.

As an alternative approach, flexible conductive composite materials were previously developed by coating PANI layers onto flexible polymeric films, which were expected to combine the sensing properties of PANI with the mechanical flexibility of polymeric substrates [25–27]. In-situ chemical polymerization can be used to form thin PANI layers on the surface of flexible polymeric substrates which can improve the effective surface areas to a certain degree. To cite an example, Patil et al. [17] developed a flexible polyester-PANI based ammonia sensor through in-situ polymerization, and the sensor exhibited a fast and stable response to ammonia. However, the sensing performance was still far less than that of the PANI nanofibers earlier mentioned. This

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might be attributed to the formation of regular PANI particles instead of interconnected PANI nanofibers by the conventional in-situ polymerization [23]. Thus, the development of flexible ammonia sensors with both high sensitivity and good mechanical flexibility remains a big challenge.

In this work, we have successfully coated interconnected nanofibers of PANI onto flexible poly(styrene-butadiene-styrene) (SBS) fiber using the in-situ dilute polymerization method. Such nanostructured PANI/SBS composite fiber not only possess high active surface areas but facilitate easy access of target gas chemicals as well as high flexibility. Due to the unique structure, the composite fiber exhibited remarkable sensitivity (5.8 for 25 ppm, 16.4 for 100 ppm), fast response (≤ 13 s), good reproducibility as well as excellent mechanical reliability. In particular, the gas sensor possesses an ultra-low detection limit at 0.1 ppm of ammonia gas at room temperature. Additionally, the SBS/PANI fiber was integrated into a commercial respirator and connected with electronic components to demonstrate practical application in detecting ammonia gas.

2. Experimental

2.1. Materials and reagents

Commercially available SBS D1102 K triblock copolymer with a butadiene/styrene weight ratio of 72/28 and a density of 0.94 g cm^{-3} was purchased from Kraton, USA. Aniline, ammonium persulfate (APS), and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All reagents were of analytical grade and used as received without further purification. Ammonia (purity: 99.99%) gas was purchased from Shanghai Chenggong gas Co. Ltd.

2.2. Sample preparation

Flexible SBS fibers were fabricated by wet spinning (see Supporting information for detailed descriptions). In-situ dilute polymerization was used to grow PANI layers on the surface of flexible SBS fibers using APS as oxidant and 1 M hydrochloric acid as dopant [28]. Typically, 0.1 g SBS fibers were immersed into 50 mL aniline/1 M dopant acid solution for 1 h at room temperature and then APS/1 M dopant acid solution was quickly added. The polymerization was carried out without disturbance for 6 h at 0–5 °C temperature. The molar ratio of aniline monomer to APS was kept at 1, and the initial concentrations of aniline/APS based on the total volume of reaction mixture were varied from 0.01 M to 0.1 M. Finally, the fibers were washed with a large excess of aq. HCl (M) under ultrasonic treatment for 10 min (SK1200H, with the power of 50 W and working frequency of 53 kHz, Shanghai Kudos Ultrasonic Instrument Co. Ltd., China) and dried in vacuum at room temperature for at least 48 h at which time the resistance was constant [29].

In this paper, samples are denoted as SBS/PANIx for simplification, where x represents the initial concentration of aniline. For instance, SBS/PANI$_{0.01M}$ represents the composite fiber prepared with aniline concentration of 0.01 M.

2.3. Structural and mechanical characterization

The surface and cross-sectional (fractured in liquid nitrogen) morphologies of the samples were characterized by field-emission scanning electron microscopy using a JEOL JSM-4800LV. The samples for SEM observation were sputter coated with platinum. The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of pure SBS fiber and SBS/PANI composite fiber were recorded on Nicolet 6700 FT-IR spectrophotometer with variable angle horizontal ATR accessory, on which a 45° rectangle ZnSe crystal was used. Tensile measurements were carried out at a constant tensile velocity of 20 mm min^{-1} with a gauge length of 5 mm on a fiber tension tester (Changzhou Dahua

Electronic Instrument Co., Ltd., China).

2.4. Sensing characterization

To investigate the sensitivity, reversibility, and reproducibility of the flexible PANI fibers upon exposure to ammonia, the fiber was placed in a 1 L chamber with a gas inlet/outlet maintained at a standard atmospheric pressure. The corresponding amount of ammonia was injected into the chamber using micro-injector. The sensor was first exposed to ammonia for a period of time, then the sensors was removed from the chamber and exposed to air. This process was repeatedly performed for several times. The resistance changes of SBS/PANI fibers were simultaneously monitored with a Keithley 6487 picoammeter. All sensing measurements were carried out at room temperature (20 °C) and 65% relative humidity.

The responses of the flexible SBS/PANI sensor are reported as $\Delta R/R_0$, where $\Delta R = R_{ex} - R_0$, R_0 is the initial resistance prior to any exposure to ammonia, and R_{ex} is the maximum resistance upon exposure to ammonia. The response time is defined as the time required for the change in signal to reach within $1/e$ (e is the EULER number) of maximum resistance value in presence of ammonia [24].

3. Results and discussions

3.1. Structure and morphology

The cross section of solution-spun fibers has an irregular non-spherical flattened shape in dimension of ca. 50 μm times 250 μm with a smooth surface (Fig. S2, Supplementary information), as shown in Fig. 1a. The SBS/PANI fibers were fabricated though in situ polymerization of aniline on the surface of pure SBS fiber. The surface and cross-section SEM images of SBS/PANI fibers prepared with different concentration of aniline are shown in Fig. 1b-j. As can be seen from Fig. 1b, the SBS fiber is uniformly covered by a thin PANI layer, indicating a skin-core structure. It is observed that the lower concentration of aniline (0.01 M) has a higher likelihood to form interconnected PANI nanofibers (Fig. 1c, Fig. S3) than the polymerization starting from higher concentration where dense PANI nanoparticles, rather than interconnected fibers, were observed (Fig. 1e, g, i). For the sample of SBS/PANI$_{0.01M}$, a top view of the SBS/PANI fiber shows highly uniform interconnected PANI nanofibers, and the diameters of the nanofibers ranged from 20 nm to 50 nm (Fig. 1c). Moreover, close inspection of the cross-sectional morphologies showed that the PANI nanofibers were rooted on the surface of the flexible SBS fibers. The adhesion between the SBS fiber and PANI is believed to have originated from the strong π-π* stacking interaction of phenyl groups of SBS and PANI [30]. Only at thick layers delamination of the PANI layer from the fiber matrix appears during cryo-fracturing (Figs. 1b, j).

The morphological evolution of deposited PANI film can be explained by using the classical theory of nucleation and growth, that is, PANI morphology depends on the mechanism of nucleation followed by growth. Elongated form (e.g., fiber or rods) is established as the growth rate for PANI is distinctly not identical in all directions (anisotropic growth). According to the mechanism proposed by Chiou [28], there are two possible nucleation sites during the process of in situ polymerization of aniline. Bulk solution and solid substrates, and these two sites compete. More specifically, when very dilute aniline/oxidant is used, the nanofibrils are initially formed on solid substrates, and those nanofibrils can continuously grow and elongate in one direction to form nanofibers. Further, in dilute polymerization, a larger amount of polyaniline can be continuously deposited onto the active nuclei resulting in interconnected 3D network structures of PANI nanofibers. In contrast, when concentrated aniline/oxidant is used, the PANI nanofibrils formation rate in bulk solution will be similar or faster than deposition rate on solid substrates [28]. A large number of PANI nanofibrils form in bulk solution and precipitate on solid substrates, then