Research paper

A flexible and disposable poly(sodium 4-styrenesulfonate)/polyaniline coated glass microfiber paper for sensitive and selective detection of ammonia at room temperature

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ABSTRACT

Ammonia (NH_3) gas monitoring is of outmost importance, once its emission above toxic levels in poultry farms can cause environmental pollution and also pose a threat on the quality of livestock, affecting the poultry production and health. Herein we report on the development of a low cost, flexible and disposable sensor device (GFP@PSS/PANI) for sensitive and selective ammonia detection at room temperature. Specifically, the sensing platform was composed by a glass microfiber paper (GFP) coated with poly(sodium 4-styrenesulfonate) (PSS) through drop-casting and polyaniline (PANI) through in situ polymerization. Various techniques including SEM and FTIR were employed to characterize the as-prepared sensing materials. Upon exposure to ammonia, the developed sensor device shows a rapid, sensitive and reversible response with a limit detection of 125 ppb and good selectivity against other common interferents such as nitrogen dioxide and carbon monoxide, most commonly found in poultry farm environment. This study provides a simple method to prepare a unique room-temperature ammonia sensing platform of low-cost and high performance, which is suitable for monitoring and controlling ammonia level in poultry farms.

1. Introduction

Ammonia (NH_3) emission has been a subject of great concern once it is a prominent air pollutant that facilitates the formation of particulate matters and also is responsible for eutrophication of the ecosystem [1–3]. The emission of NH_3 can occur from many sources, but livestock production of beef, swine and poultry is one of the major causes of ammonia emissions in the atmosphere, being responsible for 70–90% of total ammonia emission in the United States [4–6]. Besides its harmful environmental impact, high concentration of ammonia also poses a serious problem on the quality of livestock production [7]. Taking poultry farms as an example, ammonia emitted in closed poultry houses can be accumulated and reach toxic concentrations, which can negatively affect the poultry growth and its immunological response [8–10]. Therefore, the general practices nowadays to control ammonia levels in

poultry farms include good housekeeping, litter management and continuous air ventilation systems [11]. In this regard, there is an urgent need to develop low-cost but sensitive and selective sensors for monitoring ammonia concentration, thus maximizing the efficiency of the aforementioned practices in controlling ammonia level in poultry farms.

In the past decade, a number of ammonia sensors have been developed [12–16]. A variety of functional materials have been employed as the NH_3 sensing elements including inorganic oxides, carbon nanotubes, conducting polymers and composites [17–25]. Recently Xu et al. [26] presented an ultrathin composite film composed of layered double hydroxide (LDH)/polyaniline (PANI) for ammonia detection with high sensivity, high selectivity and rapid response/recovery time, which is attributed to a synergic effect between LDH and PANI. As a conducting polymer, PANI is an outstanding candidate in ammonia sensor

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applications, once its produced by a simple and cost effective route and also possesses good mechanical flexibility [27]. Furthermore, Zhang et al. [28] employed electrospun PANI nanofibers doped with (+)-camphor-10-sulfonic acid to construct a high-performance resistor-type gas sensor for NH_3 and NO_2 detection by taking the advantage of the high surface area of PANI nanofibers. However, the sensor responds to both NH_3 and NO_2, indicating the need of further improvement of the sensor's selectivity.

Here, a glass microfiber paper (GFP) was employed as a supporting substrate to prepare a flexible, disposable and low-cost room-temperature NH_3 paper sensor for highly sensitive and selective detection of NH_3. *In situ* coating of the sensing platform consisting of PSS and PANI on glass microfiber paper (denoted as GFP@PSS/PANI) was realized by *in situ* drop-casting of PSS and *in situ* polymerization of PANI in sequence. Various techniques including SEM and FTIR were employed to characterize the composite. The flexible GFP@PSS/PANI was then employed to fabricate a resistor-type NH_3 sensor which is operated at room temperature. Upon exposure to ammonia, the developed sensor device showed a rapid, sensitive and reversible response with good selectivity against other common interferents such as nitrogen dioxide and carbon monoxide. A sensing mechanism was also proposed to illustrate the excellent sensing performance using GFP@PSS/PANI composite.

2. Materials and methods

The flexible sensor devices were fabricated through an *in situ* dip-coating and polymerization process on GFP substrate. The glass microfiber paper (Whatman™ 934-AH™ Glass Microfiber filter) was purchased from GE Healthcare Bio-Sciences Corp. Aniline ($C_6H_5NH_2$, 99.5%) and ammonium persulfate (APS − $(NH_4)_2S_2O_8$, 99.99%) and poly(sodium 4-styrenesulfonate) (PSS − $M_w \sim 200,000$) were purchased from Sigma Aldrich.

To prepare the sensor devices, $0.04 \, mol \, L^{-1}$ of aniline, $0.05 \, mol \, L^{-1}$ of APS and $0.1 \, mol \, L^{-1}$ of PSS were prepared individually. Then the three solutions were loaded on the GFP substrate in different sequence to prepare different sensor devices in order to compare their sensitivity to ammonia gas and thus optimize the fabrication procedure. The first device (GFP@PANI) was obtained by APS addition as oxidant agent for *in situ* polymerization of aniline on glass microfiber paper. *In situ* polymerization of PANI was observed and confirmed by the color change of GFP substrate from colorless to greenish color. The second device (GFP@PANI/PSS) was obtained as the first one with an additional step of drop-casting of PSS on the top of GFP@PANI. The third device (GFP@PSS/PANI) was obtained by drop-casting of PSS on GFP substrate followed by PANI polymerization in sequence. The loading volume of PSS, Aniline and APS in the procedure is 50 mL each. The devices were left to dry under ambient conditions for 12 h. To complete the fabrication of the resistor-type NH_3 sensor, two conducting carbon tapes were placed on the as-prepared sensing films (gap of 4 mm) to function as electrical contacts. Fig. 1 shows the schematics of the sensor device.

In order to confirm the successfully PANI polymerization and PSS coating on the glass microfiber paper, the Fourier Transform Infrared

(FTIR) spectra were recorded with a Nicolet Magna-IR 560 spectrometer. The surface homogeneity and uniformity of polymer coating on GFP substrate were characterized using a JEOL 6335F field-emission scanning electron microscope (FESEM). Gas sensing test system was assembled connecting the sensor platform in a closed tube chamber with gas inlet and outlet ports for gas flow control. The gas flow rate was set as $3 \, L \, min^{-1}$ for the carrying synthetic air and gas mixtures (NH_3/synthetic air) were regulated by a computer-controlled gas mixing system (S-4000, Environics Inc., USA). 1 V DC bias was supplied to the sensor platform through the two conducting carbon electrodes and the sensor response (current) was continuously monitoring using a CHI 660D electrochemical analyzer (CH Instruments Inc., USA). Prior to the measurement, the carrying gas was purged for 20 min in order to obtain a stable baseline. For 100 ppm NH_3 sensing experiment, the sensor was exposed to NH_3 for 2 min followed by 3.5 min in synthetic air as recovery time, and then the procedure was repeated for multiple cycles. The calibration curve for several NH_3 concentrations was obtained with 4 min of NH_3 gas exposure and 15 min of recovery time. The current in the sensor was continuously measured during the gas flow cycles. The electric resistance of the sensor was calculated by applying Ohm's Law ($R = V/I$) and the resistance variation observed could be directly related to the ammonia concentration and normalized as $\Delta R/R_0\% = [(R_g-R_0)/R_0] \times 100\%$, where R_0 is the electrical resistance of the sensor in synthetic air and R_g is the measured resistance in NH_3.

3. Results and discussion

The flexible polymer-coated glass microfiber paper was carried out by drop-casting and/or *in situ* polymerization in different sequence. PSS coating can be achieved through drop-casting, while PANI coating can be realized by using APS as an oxidant to trigger the polymerization of aniline. In this study, APS solution was dropped on the substrate before aniline solution, thus creating an oxidizing surface and improving the polymerization and adhesion of PANI on the substrate (Fig. 1). The rationale to incorporate PSS in the sensing composite relies on the fact that gas sensors having PSS in the composition have demonstrated superior gas sensing reversibility [29–31]. In this study, PSS was coated in different ways (either under or on PANI layer) to investigate its effect on the sensing performance for different composites, which will be discussed in subsequent section.

The successful coating of PANI can be first observed and confirmed by the visual color change of the substrate from colorless to greenish color. The formation of PANI on the substrate was further confirmed by the FTIR spectra (Fig. 2). The vibrational modes related to PANI were observed for GFP@PANI, GFP@PANI/PSS, and GFP@PSS/PANI. The peak at $1487 \, cm^{-1}$ is ascribed to the stretching vibration of C=C benzenoid rings and the peak at $1128 \, cm^{-1}$ to the stretching vibration of C=C quinonoid ring while the peak at $1011 \, cm^{-1}$ is assigned to in-plane benzene ring bending vibration [32]. The PSS coating layer on the substrate was also confirmed by FTIR spectra where PSS vibrational modes were observed for GFP@PANI/PSS and GFP@PSS/PANI at $1184 \, cm^{-1}$ corresponding to asymmetric stretching of SO_3^- group [33]. As a comparison, a sample of GFP coated with pure PSS was also
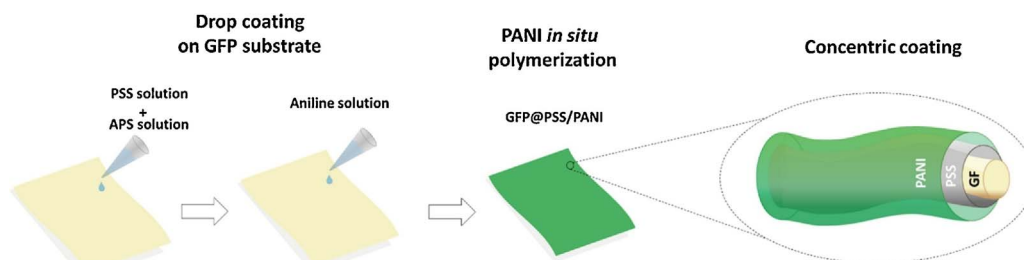
Fig. 1. Schematic drawing of the GFP@PSS/PANI device fabrication.