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Using a PEDOT:PSS modified electrode for detecting nitric oxide gas

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ABSTRACT

PEDOT:PSS thick films, prepared by the drop-coated method, were used in this study for sensing nitric oxide (NO) gas. The thickness of PEDOT-PSS film was controlled by dropping different volumes of PEDOT-PSS solution to improve the response of PEDOT-PSS film. Due to its porous structure, the thicker the PEDOT-PSS film is, the higher the noticeable surface area. Thus, a larger response is found. However, since the concentration of NO gas used was low (10 ppm), the effect of the surface area was not noticeable when the thickness of the film was greater than 5 μm. In the range of 2.5–10 ppm NO, the relationship between the response of the PEDOT-PSS film and the NO concentration was linear. The limit of detection ($S/N = 3$), response time (t_{95}), and recovery time (t_{95}) were about 350 ppb, 527 s, and 1780 s, respectively. The response of PEDOT-PSS film to 10 ppm NO gas was dramatically affected by the presence of either O_2 or CO. The standard deviation, with respect to the sensitivity of the NO gas sensor based on PEDOT:PSS film, was 2.2%. The sensitivity of the sensor remained at about 74.5% that of a fresh one.

1. Introduction

Nitric oxide (NO) is one of the toxic air pollutants generated from every combustion process. This compound plays an important role in the atmospheric reactions that create the ozone (O_3), the major component of smog, and acid rain [1]. According to regulations of the Occupational Safety and Health Administration (OSHA), the permissible exposure limit is set at 25 ppm (TWA).

Several techniques, including electrochemical methods, gas phase chemiluminescence [2], fluorescence [3], conductometry [4], and electron magnetic resonance spectroscopy [5], have been proposed for the detection of NO gas. Among them, metal oxide gas sensors, based on the principle of conductometry, attract much attention due to real-time measurement in the gas phase, the small size, easy fabrication, and low cost. However, to achieve higher sensitivity to the analytes, the normal operation temperature of the metal oxide based gas sensor is rather high (>300 °C), which requires high-energy consumption.

Recently, conducting polymers, such as polythiophene, polyaniline, and polypyrrole, have become an attractive class of materials for gas sensing applications [6–9]. They can be easily synthesized by a simple synthesis procedure, and especially, they can detect the analyte gases with satisfactory sensitivity at room temperature. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising conducting polymers due to its high conductivity and excellent environmental stability [10]. Although PEDOT itself cannot be easily cast into film due to its insoluble property, PEDOT doped with poly(styrene-sulfonate) can be dispersed well in the aqueous solution, which facilitates the film fabrication. Prinstine PEDOT or doped PEDOT has been used as the sensing material for the detection of HCl [11], NH_3 [12], NO_2 [13], and alcohols [14] and some volatile organic compounds [15]. However, to our knowledge, the NO sensing characteristics of the PEDOT:PSS film based gas sensor have never been reported yet.

In this study, a simple drop-coated method was employed to prepare PEDOT:PSS film. The effects of the film thickness, the working temperature, NO concentration and the presence of some potential interfering gases on the sensing response of the PEDOT:PSS to NO gas were investigated.

2. Experimental

2.1. Preparation of the PEDOT:PSS thick film

An aqueous suspension of the PEDOT:PSS (Baytron®P VP Al 4083, H.C. Starck GmbH & Co. KG) was purchased from Bayer and used as received. The concentration of the PEDOT:PSS suspension was 1.3–1.7 wt%. To prepare the PEDOT-PSS film-modified electrodes, a specific volume of PEDOT:PSS solution was drop-coated onto an Al_2O_3 substrate with screen-printed

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interdigitated gold electrodes, and then vacuum dried at 70 °C overnight.

The film thickness was determined by a Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-6700F, Japan).

2.2. Gas sensing experiment

The gas sensing measurements were carried out in a closed glass chamber. The sensing film, facing against the gas inlet at a flow rate of 250 ml/min, was placed in the sensing chamber. To alleviate the baseline drift, the sensing films were exposed to ultrapure N_2 (ShenYi Gas Co., Taiwan, 99.9995%) overnight before data collection. The transient resistance responses of the PEDOT-PSS film to 10 ppm NO gas, at different working temperatures, tuned by mixing 50 ppm NO (ShenYi Gas Co., Taiwan, 99.99%) with ultrapure N_2 gas stream from a tank through a flow meter, were obtained by applying a 1.0 V DC across both terminals of the electrodes. The current responses were recorded by a potentiostat (CHI 440) and converted into resistance according to Ohmic law. The response, S, is defined by the following equation

$$S = \frac{(R_g - R_{N_2})}{R_{N_2}} \times 100\% \quad (1)$$

where R_{N_2} and R_g are the resistances of the film in N_2 gas and in test gas, respectively. The calibration curve of NO concentration was constructed after collecting the responses of the PEDOT:PSS film to various NO concentrations ranging from 10 to 2.5 ppm.

To test the interferences of O_2, CO, and NO_2, PEDOT-PSS films were exposed to the gas mixtures of O_2 (21%) and NO (10 ppm), NO_2 (10 ppm) and NO (10 ppm), and CO (10 ppm) and NO (10 ppm) until the responses became stable. The purities of both CO and NO_2 gases were 99.9% (ShenYi Gas Co.). The films were then exposed to ultrapure N_2 gas until the responses were recovered.

3. Results and discussions

3.1. Temperature effect

Fig. 1 shows the general responses of the PEDOT:PSS thick film (~4.5 μm) to 10 ppm NO gas at room temperature. It was found that the response decreased at the beginning cycles and stabilized after five cycles of exposure to NO gas. Some possible interfering gases, such as water vapor, O_2, and CO_2, could adsorb in the PEDOT:PSS film, and thus the initial responses were affected. Therefore, a cleaning procedure for the PEDOT:PSS film is necessary before the sensing test.

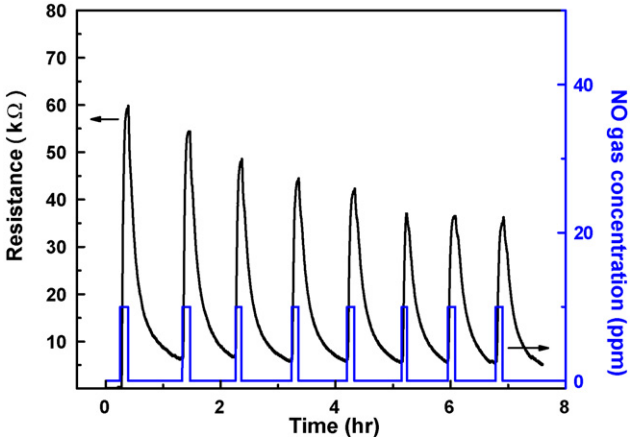

Fig. 1. Transit responses of the PEDOT:PSS film to 10 ppm NO gas at room temperature. The film thickness of the PEDOT:PSS film: ~4.5 μm.

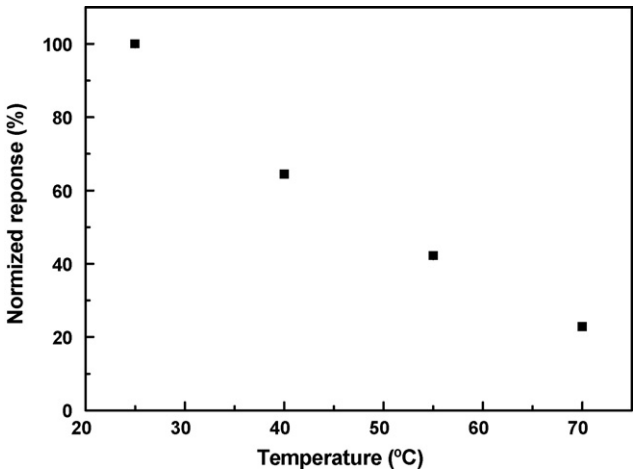

Fig. 2. Temperature dependence of the normalized response of the PEDOT:PSS film to 10 ppm NO gas. The film thickness of the PEDOT:PSS film: ~4.5 μm.

Unlike the gas sensors based on metal oxide, the gas sensors based on PEDOT-PSS thick film usually operate at rather low temperatures. In this study, the optimal working temperature for the detection of NO gas was found to be room temperature (see Fig. 2). Since the interaction between PEDOT:PSS film and NO gas is exothermic, the activation energy of the desorption is larger than that of the adsorption. Although the increase in temperature favors both the adsorption and the desorption processes, higher temperature should favor the process with a higher activation energy. This explains the results revealed in Fig. 2 that the decrease in response at higher temperatures is resulted from the higher desorption rate of NO gas.

Several sensing mechanisms have been proposed for the conducting polymer systems, including the redox reactions between the polymer and the analyte, partially charge transfer between the polymer and the analyte, and polymer swelling [16]. In this study, due to the chemical nature of NO gas, the observed increase in the sensor resistance could be attributed to the redox reaction or the charge transfer. NO gas is known to be a highly active and electron-donating free radical [17], and therefore, upon electron transfer from NO to the partially positive charged sulfur site on the backbone of the p-type PEDOT:PSS, the charge carrier concentration on the polymer backbone decreases, resulting in the increase in the resistance of the PEDOT:PSS film.

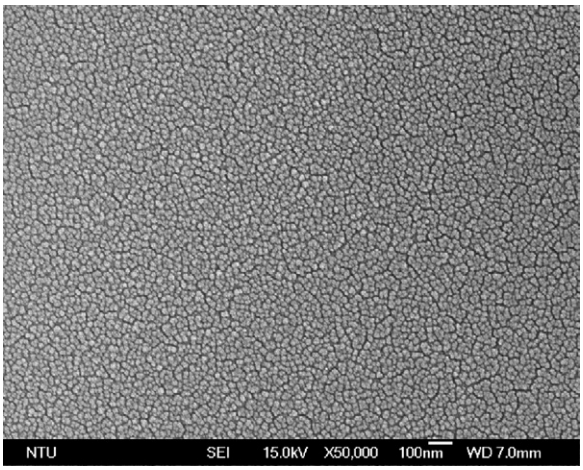

Fig. 3. The top-view of SEM image for the PEDOT:PSS film with a film thickness of 4.5 μm.