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.

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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 tem-

perature. 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

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

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

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.
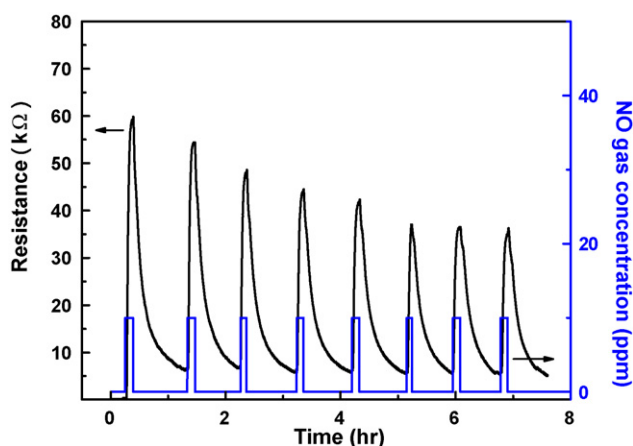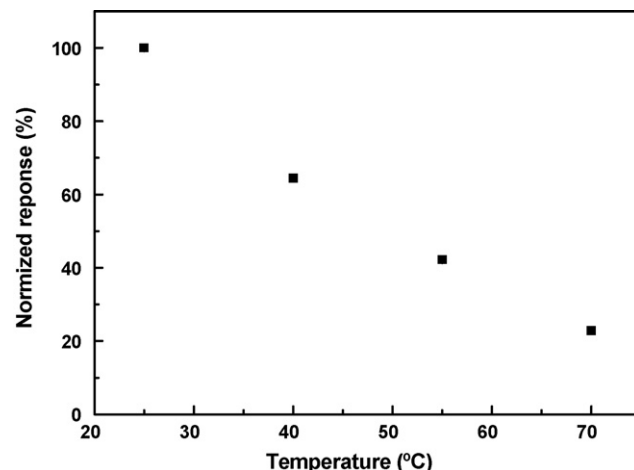

Fig. 2. Temperature dependence of the normalized response of the PEDOT:PSS film to 10 ppm NO gas. The film thickness of the PEDOT:PSS film: ∼4.5 μm.

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.
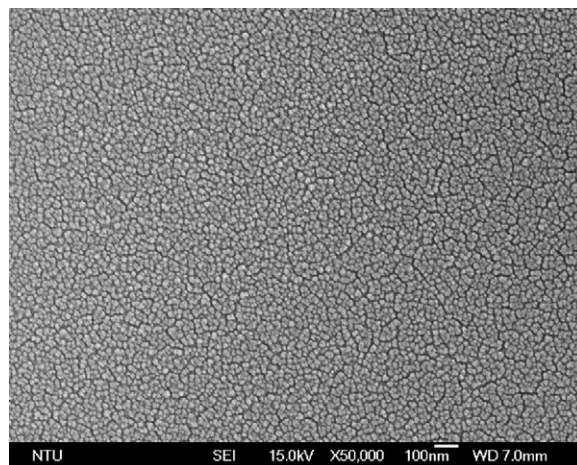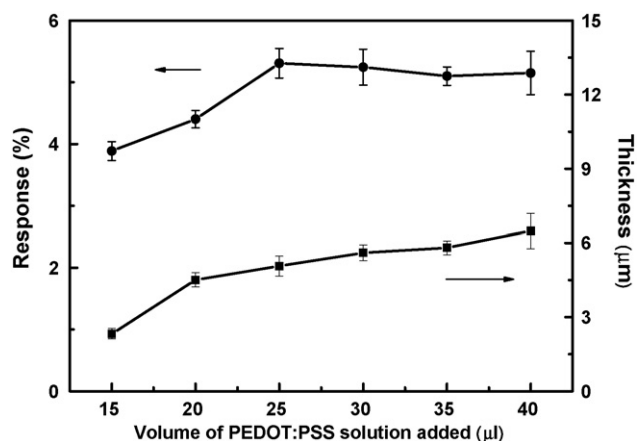

Fig. 1. Transit responses of the PEDOT:PSS film to 10 ppm NO gas at room temperature. The film thickness of the PEDOT:PSS film: ∼4.5 μm.

Fig. 3. The top-view of SEM image for the PEDOT:PSS film with a film thickness of 4.5 μm.
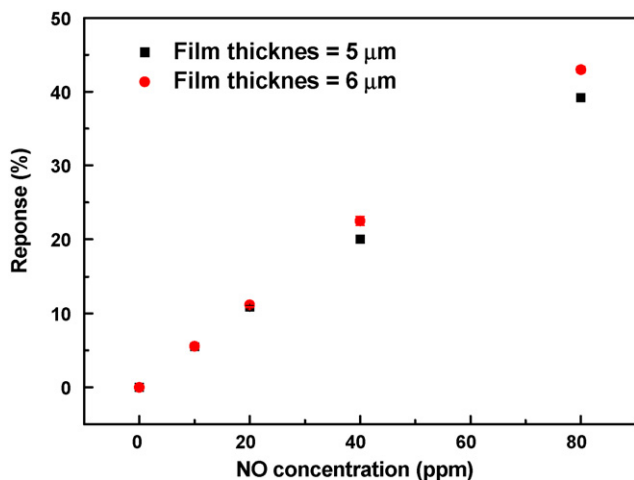
Fig. 4. The responses of the PEDOT:PSS films with different thickness, controlled by dropping different volumes of the PEDOT:PSS solution, to 10 ppm NO gas at room temperature.

3.2. Thickness effect

The SEM picture is shown in Fig. 3, indicating the nanoporous nature of a PEDOT:PSS film. Due to its porous structure, the surface area for NO gas adsorption would increase as the thickness of PEDOT-PSS film is increased. Therefore, the sensor response would be improved if the thickness of PEDOT-PSS film is optimized. Fig. 4 shows the responses of the PEDOT-PSS films, with different thicknesses, to 10 ppm NO gas at room temperature. It should be noted that the average values of the thickness of the PEDOT:PSS film were determined by SEM measuring at least three spots on the same substrate. As seen, the sensor response increases as the thickness of the PEDOT-PSS film increased from 2.3 to 5.0 μm, and became saturated at a thickness greater than 5.0 μm. The available surface area was larger at higher film thicknesses, but the concentration of NO gas (10 ppm) used here might be so low that the effect of the surface area was not noticed. Indeed, at higher NO concentrations (>40 ppm), as shown in Fig. 5, the film thickness (or the surface area) plays an important role on the sensor response. Therefore, for detection of rather low NO concentrations (<10 ppm), we chose PEDOT:PSS film with a thickness of 5 μm for later experiments.

3.3. Gas characteristic of the PEDOT:PSS film

The responses of the PEDOT-PSS film as a function of NO gas concentration are shown in Fig. 6. All responses increased linearly with
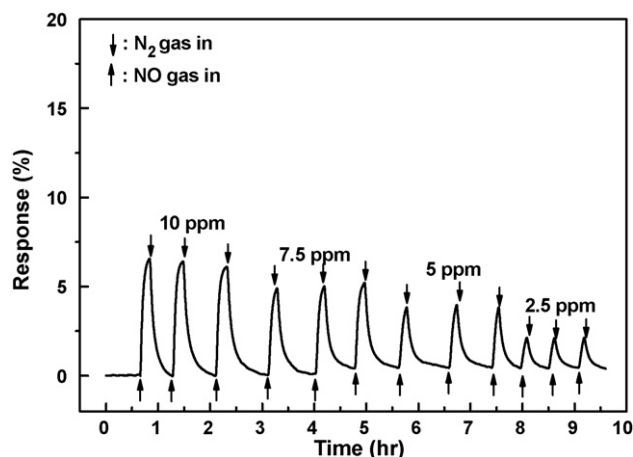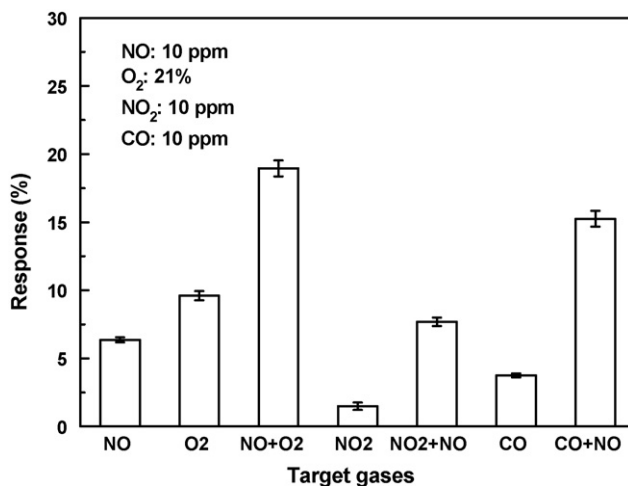

Fig. 6. The responses of the PEDOT:PSS film to various NO gas concentrations. The inset shows the calibration curve. The film thickness of the PEDOT:PSS film: ~5 μm.

the increase in the concentration of NO. The sensitivity, defined as the response divided by the concentration (in 1/ppm) of the gas sensor based on the PEDOT-PSS film is about 0.65%/ppm. The limit of detection, based on the signal-to-noise ratio of 3 ($S/N = 3$), for PEDOT-PSS film was found to be about 350 ppb. The response time (t_{95}) and recovery time (t_{95}) were calculated to be 527 and 1780 s, respectively, which were comparable to other gas sensors based on the PEDOT thick films [14], and were large compared to that based on the PEDOT-PSS nanowires [18]. It could be inferred that the improved response by the increase in the film thickness would slow down the response and recovery of the sensor.

To simulate the environmental air quality monitoring, 21% O_2, 10 ppm NO_2 and CO gases were selected as the interfering species. As shown in Fig. 7, the sensor resistance increased as it was exposed to these analyte gases. Besides, the response of PEDOT-PSS film to 10 ppm NO gas was affected dramatically in the presence of 21% O_2 or CO gas. It was noticed that the sensor responses to "NO + O_2" and "NO + CO" were higher than the superposition of "NO" and "O_2", and "NO" + "CO", respectively. According to the analytical gas report provided by the gas supplier, both air and carbon monoxide tanks have very small amounts of impurities, for example, H_2O (3–5 ppm) and CO_2 (<1 ppm), which could cause some side reactions upon mixing with NO gas. Thus, the products generated by the side reaction may cause additional signal when interacting with the PEDOT:PSS film. On the other hand, NO_2 had minor effects on the sensor responses

Fig. 5. The responses of the PEDOT:PSS films with thicknesses of 5 and 6 μm against various NO concentrations ranging from 10 to 80 ppm.

Fig. 7. The responses of the PEDOT:PSS film to 21% O_2, and 10 ppm NO, NO and CO gas alone, and mixtures of 10 ppm NO and 21% O_2, 10 ppm NO and NO_2, 10 ppm NO and CO. The film thickness of the PEDOT:PSS film: ~5 μm.
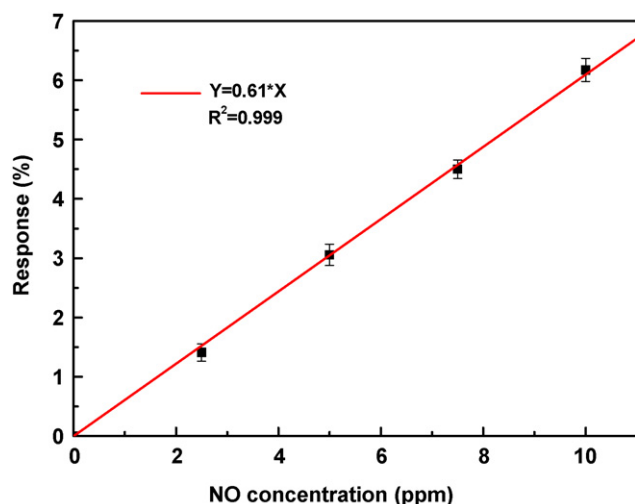
Fig. 8. The calibration curves of the fresh three PEDOT:PSS modified electrodes at room temperature. The film thickness of the PEDOT:PSS film: ∼5 μm.

compared to CO and O_2 gases. To improve the selectivity of the PEDOT:PSS film against O_2 and CO gases for the real world application, some dopants sensitive to NO gas could be incorporated into the film. This includes cytochrome *c* and bis[2,9-dimethyl-1,10-phenanthroline] copper (II) complex, whose reactivity to NO gas
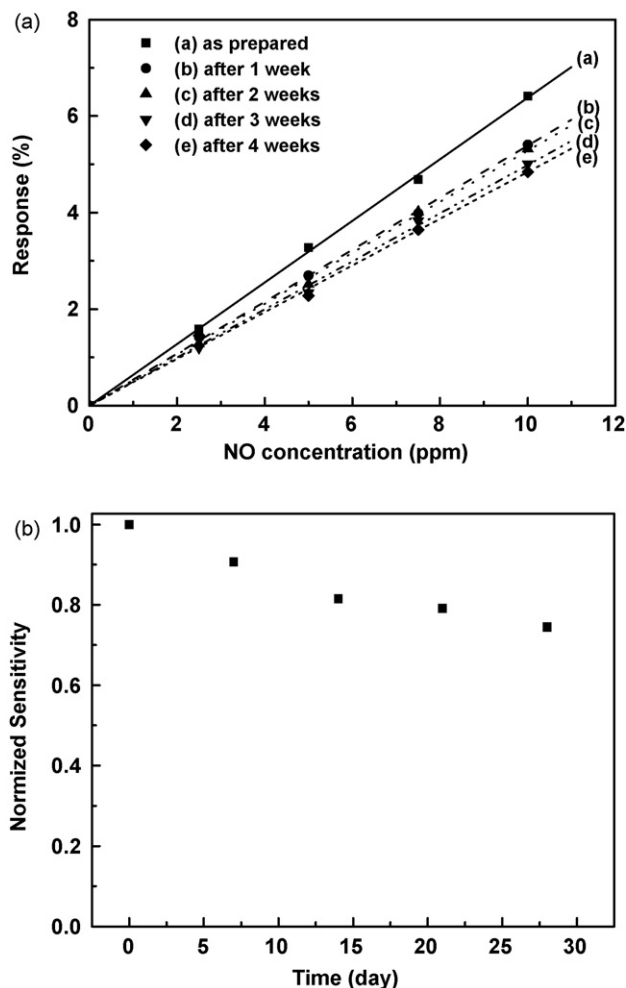

Fig. 9. (a) The calibration curves of the PEDOT:PSS modified electrode obtained for different periods. (b) Time dependence of the normalized sensitivity for the PEDOT:PSS modified electrode. The film thickness of the PEDOT:PSS film: ∼5 μm.

has been proven in the literature [19,20]. Using these materials and finding other suitable dopants are under investigation now.

The issue of the PEDOT:PSS film prepared by drop-coating is film uniformity, which could result in poor reproducibility of sensor performance. Fig. 8 shows the calibration curves for three fresh electrodes at room temperature. As seen, the standard deviation, with respect to the sensitivity of these three electrodes, was about 2.2%, which was quite satisfactory.

Fig. 9 demonstrates the long-term stability of the sensor within a month. The electrode was tested once a week and was stored in a box after the sensing test. The box was exposed to the ambient air at room temperature with a relative humidity of 45%. It was found that the sensitivity decreased as time went by, and the sensitivity of the electrode after one month remained 74.5% that of the fresh one, as seen in Fig. 9 (a) and (b).

4. Conclusion

The PEDOT:PSS film-modified electrodes were fabricated and their sensing characteristics towards NO gas were investigated. The standard deviation, with respect to the sensitivity of the PEDOT:PSS based gas sensor, was 2.2%. The PEDOT:PSS film showed the highest response to NO gas at room temperature. The sensor responses increased as the PEDOT:PSS film thickness was increased from 2.3 to 5.0 μm. The limit of the detection for the PEDOT:PSS based NO gas sensor was 350 ppb, which was suitable for indoor monitoring of NO. However, the sensor response was significantly affected by the presence of either O_2 or CO. The sensitivity of the PEDOT:PSS based gas sensor, after about one month remained at 74.5% that of a fresh one.

Acknowledgement

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Kuo-Chuan Ho received B.S. and M.S. degrees in Chemical Engineering from the National Cheng Kung University, Tainan, Taiwan, in 1978 and 1980, respectively. In 1986, he received his Ph. D. degree in Chemical Engineering at the University of Rochester. The same year he joined PPG Industries, Inc., first as a Senior Research Engineer and then, from 1990 until 1993, as a Research Project Engineer. He has worked on the electrochemical properties of various electrode materials, with emphasis on improving the performances of sensor devices. Following a six-year industrial career at PPG Industries, Inc., he joined his alma mater at National Cheng Kung University in 1993 as an Associate Professor in the Chemical Engineering Department. In 1994, he moved to the Department of Chemical Engineering at National Taiwan University. Currently, he is a Professor jointly appointed by the Department of Chemical Engineering and Institute of Polymer Science and Engineering at National Taiwan University.