

Examining the Use of TiO₂ to Enhance the NH₃ Sensitivity of Polypyrrole Films

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ABSTRACT: Polypyrrole/Titanium dioxide (PPy/TiO₂) composite thin films were prepared by polymerizing the monomer pyrrole in aqueous solution containing a certain amount of TiO₂ particles at room temperature, and their response to ammonia (NH₃) gas was examined systematically. Compared with the pristine PPy film, which reached the saturation at the concentration of NH₃ beyond 200 ppm, the composite films showed more stable response and higher sensitivity. Furthermore, the PPy/TiO₂ com-

posite thin films exhibited a low detection limit of 2 ppm. The film thickness, which had a strong influence on the film sensitivity to NH₃, could be controlled by varying the polymerization time. The sensitivity to NH₃ gas of the samples with different content of TiO₂ and different molar ratio of PPy/TiO₂/oxidant was studied. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3351–3356, 2010

Key words: composites; films; polypyrroles; sensors

INTRODUCTION

The environmental importance is well understood, and much research has focused on the development of suitable gas-sensitive materials. The conventional gas sensors based on the oxide have a good sensitivity; however, they are usually operated at high temperature, and thus great energy was consumed.^{1,2} Therefore, much effort has been focused on the development of the sensors operating under room temperature and with low power. The gas sensors based on conducting polymer have received considerable interest because of their superior properties such as excellent conductivity, high gas-sensing ability, and good environment stability.^{3–5} On the other hand, the oxide-based polymer composites have been reported to obtain the optimal properties in recent years, which exhibit high sensitivity to numerous kinds of gases including NH₃, vapors of organic solvents and other toxic gases, and their electrical responses were believed to involve the modification of the conductive path due to the swelling of polymer film and/or the charge transfer resulting from the interaction of adsorbed gas molecules with semiconducting oxide and conducting polymers.^{6,7} Among the various organic conductive

polymers, polypyrrole (PPy) has been studied frequently as a gas sensor owing to its excellent properties of stability and flexibility. To improve the performance of PPy film as gas sensors, several PPy-based composites have been investigated. For example, Lin et al. combined the PPy with poly(vinyl alcohol) and other insulator polymers as matrix to improve the mechanical property and sensitivity of the PPy.^{8–10} There are also some literatures reporting the great improvement achieved in sensitivity of ammonia gas vapors using PPy/oxide-iron composite films.^{11–13}

Titanium dioxide (TiO₂) is an n-type semiconductor, which has been extensively used for detecting H₂, NH₃, and SO₂ gases.^{14,15} However, the sensors based on TiO₂ require an elevated operation temperature, which may cause long-term instability. Therefore, it is desirable to develop new sensors that could be operated at room temperature while keeping the properties of TiO₂ for gas sensing. For instance, Tai et al. and Ma et al. have investigated the gas sensitivity of polyaniline/TiO₂ nanocomposite thin films.^{16,17} In this article, we prepared PPy/TiO₂ composite films by *in situ* polymerizing the monomer pyrrole in aqueous solution, which contained an appropriate quantity content of TiO₂ particles using FeCl₃ as oxidant. Different thicknesses of the pristine and composite films were obtained by controlling the polymerization time. The sensing behaviors of the films with different thicknesses to ammonia gas were investigated by using flow system.

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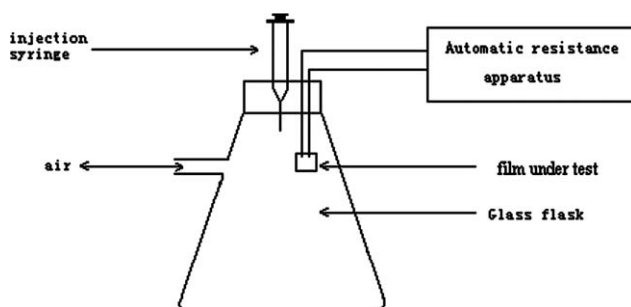


Figure 1 Schematic representation of the gas sensor test chamber.

EXPERIMENTAL

Materials

Pyrrole was distilled under reduced pressure before use, and other reagents were analytical grade and used without further purification. TiO_2 particles were synthesized by coprecipitation method and sintered at 500°C for 2 h.

Preparation of PPy/ TiO_2 composite films

PPy/ TiO_2 films were prepared by *in situ* polymerization process. A typical experiment was done as follows: 0.06 g of TiO_2 was dispersed into 50 mL of aqueous solution, which contained 0.23 g of pyrrole monomer followed by ultrasonication for 20 min. The acetone-cleaned Mylar substrate was hung with brass wires and vertically immersed into the solution mentioned above. Then, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (molar ratio of Py to $\text{Fe}^{3+} = 1 : 1$) powder was added as oxidant, and the polymerization was arisen with continuous stirring at room temperature. Then, the Mylar substrate and the powder collected from the reaction solution were washed with ethanol, acetone, and distilled water and then dried at room temperature under reduced pressure. For comparative purpose, pristine PPy film was synthesized using the same approach in the absence of TiO_2 particles.

Characterization

The thickness of the films was calculated by the relation $A_{400} = 5.4 \times 10^{-3} d_f$ (A_{400} referred to the absorption of the film at 400 nm and d_f (in nm) represented the film thickness).¹⁸ The X-ray diffraction (XRD) pattern of the powder collected from the reaction solution was taken with Cu $K\alpha$ radiation using Shimadzu XRD-6000. The detector ranged from 10° to 80° at a scanning speed of $10^\circ/\text{min}$. UV-vis spectra of the films were studied using a UV-vis spectrometer (UV-2550). The adhesion strength of composite film to Mylar substrate was evaluated by the peel adhesion test with $20 \mu\text{m}/\text{s}$ peel velocity.¹⁹

Sensitivity test

The changes of resistance with time of the sample were recorded by a home-made Automatic resistance apparatus. The relative differential resistance change of film in test was calculated using the following equation:

$$\text{Response} = \Delta R/R = (R_v - R_0)/R_0 \quad (1)$$

In the above equation, $\Delta R/R$ is the relative differential resistance change of film, R_v is the resistance when the film is upon exposure to a certain concentration of NH_3 , and R_0 is the resistance of the film before exposure.

The test chamber used in this work was designed as shown in Figure 1. The chamber consisted of a 958 mL glass flask that was sealed with a rubber bung containing a septum. The chamber was flushed with air for 2 min to remove any contaminants from the flask and stabilize the film before test. A syringe was used to inject the required volume of vapor into the chamber. Finally, the flask was flushed with air to remove the vapor and allowed to recover the baseline value of the film. The resistance changes of the samples were recorded. Each data of gas sensitivity were collected by three times measurement, and average values were calculated.

RESULTS AND DISCUSSION

Formation

The thickness of the prepared pristine PPy films and PPy/ TiO_2 composite films with different polymerization time is listed in Table I. It can be seen that the thickness of the pristine PPy films increased from 88 to 259 nm when the polymerization time ranged from 0.5 to 6 h. After 6 h, the thickness decreased to 179 nm. Similarly, the thickness of the composite films increased from 97 to 248 nm and then decreased to 183 nm when the polymerization time was prolonged. We consider that there were lots of oligomers generated at the initial polymerization process in the aqueous solution, and some of them were adsorbed onto the substrates. With the

TABLE I
The Thickness of Pristine and Composite Films at Different Polymerization Time

Polymerization time (h)	Thickness of PPy film (nm)	Thickness of PPy/ TiO_2 composite film (nm)
0.5	88	97
1	122	131
2	156	170
4	219	248
6	259	220
8	179	183

continuously polymerization of oligomers, the thickness of the PPy on the substrates increased simultaneously. The polymer on the films falls off into solution with the extension of the reaction time and results in the decrease of the thickness.²⁰ For the pristine films and PPy/TiO₂ composite films, the time to reach their maximum values of thickness is 6 and 4 h, respectively, and it be attributed to that oxide can accelerate the polymerization. In our experiments, the polymerization of pyrrole in aqueous solution, which contained a certain amount of TiO₂ particles, was directly taken on the Mylar substrate. The peel force of the typical composite film to substrate was 0.85 (± 0.02) N.

XRD

Figure 2 gives the XRD patterns of the powder after long exposition to NH₃ or not. The diffraction peaks of the composite were measured with 2θ values at 25.4°, 38.04°, 48.12°, 55.03°, and 62.5°, respectively. It can be concluded that the TiO₂ particles synthesized in our experiment were anatase. The weak peak at about $2\theta = 25^\circ$, which is in coincidence with the peak at 25.31° of TiO₂, is the typical amorphous PPy. After exposed to NH₃, the peak of 54.2 has significantly improved, and the peaks of 55.03° and 62.5° weakened, and the reason is not clear now.

Gas sensitivity

Figure 3 shows the sensitivity of the pristine PPy and PPy/TiO₂ composite film after exposure to 100 ppm NH₃ for 300 s to investigate the sensitivity and stability of the films. Obviously, the response of PPy/TiO₂ composite film to the ammonia gas is stronger than that of the pristine PPy film. The response of the composite film reaches a relatively

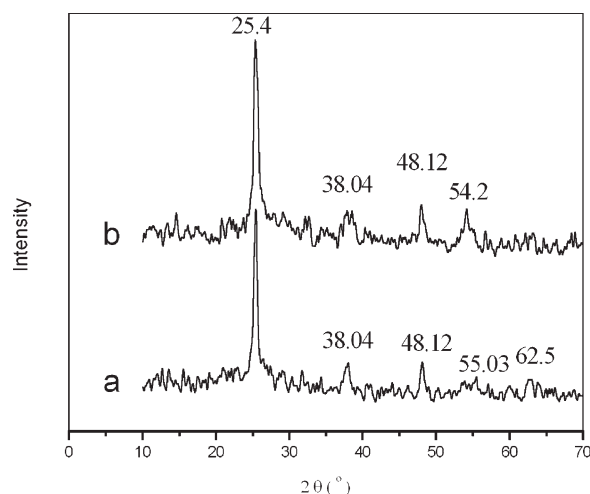


Figure 2 XRD patterns of the PPy/TiO₂ composite before (a) and after (b) exposed to 100 ppm NH₃.

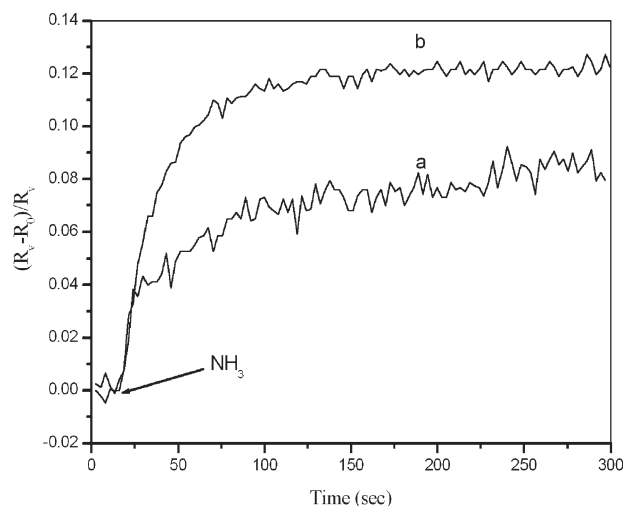


Figure 3 The response curves of pristine PPy (a) and the PPy/TiO₂ composite film (b) when exposed to 100 ppm of NH₃.

steady state quickly, but the pristine PPy film increases gradually for a long time.

The higher sensitivity in the presence of TiO₂ particles could be attributed to the higher porosity in the composite film. TiO₂ has no response to NH₃ at room temperature in our experiment. The incorporation of TiO₂ should result in a porous structure. Higher porosity usually leads to a better response because of the higher diffusion rate and higher gas adsorption. In our previous work, we have investigated the mechanism of the improvement of the sensitivity of PPy film in the presence of Fe₃O₄ nanoparticles.²¹ The increased response of the composite film to NH₃ vapor can be explained by p-n junction. As PPy is p-type conductor and TiO₂ is n-type semiconductor, we have postulated that PPy and TiO₂ form a p-n junction, and the interparticle electron transition from TiO₂ to PPy causes the reduction of the activation energy and enthalpy of physisorption for NH₃ gas and increases the performance of device. The improvement of sensitivity is then expected.²²

Figure 4 shows the response of pristine PPy and the PPy/TiO₂ composite film to NH₃ at different concentration. As shown in Figure 4, it is clear that the pristine PPy film reaches saturation, and the response increases slowly when the concentration exceeds up to 200 ppm. The response of the composite film shows a good linearity with the change of the NH₃ concentration. Furthermore, the response of composite film is 0.05 that is 10 times to the pristine one at 20 ppm of NH₃. It suggests that the composite film may have a lower detection limit than that of the pristine film. Figure 5 gives the response of the composite film at low NH₃ concentration, from which we can see that the lowest detection limit of

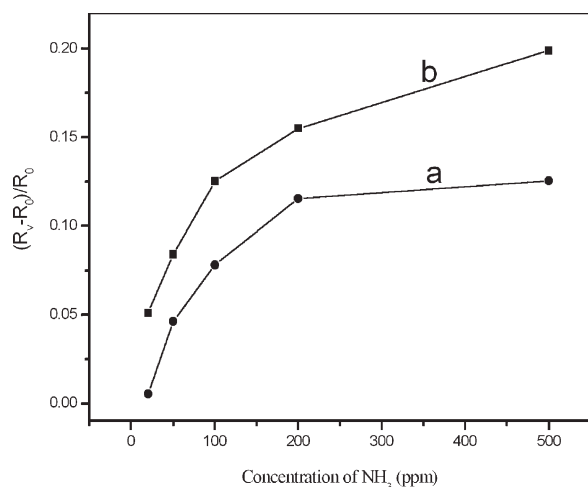


Figure 4 The response of the pristine PPy (a) and the PPy/TiO₂ composite film (b) to NH₃, the concentrations of NH₃ ranging from 20 to 500 ppm.

the composite film was only 2 ppm, and the result shows a good linearity. Compared with the gas sensitivity results of PPy composite film with other group,^{13,23} our films present the good properties, such as lower detection gas concentration and operating temperature.

The NH₃ gas sensitivity of the samples with different content of TiO₂ and different molar ratio of Py/TiO₂/oxidant is shown in Table II. The sensitivity is highest when the concentration of TiO₂ was 20% in the composite. When its concentration was less than 20%, the TiO₂ does not influence much on the sensitivity of the sample; on the other hand, when the concentration of TiO₂ was more than 20% in the composite, the relatively low concentration of Py leads to the formation of poor quality film. The molar ratio also affected the sensitivity. The best sensitivity appears in the molar ratio of 1. The pyrrole was incompletely

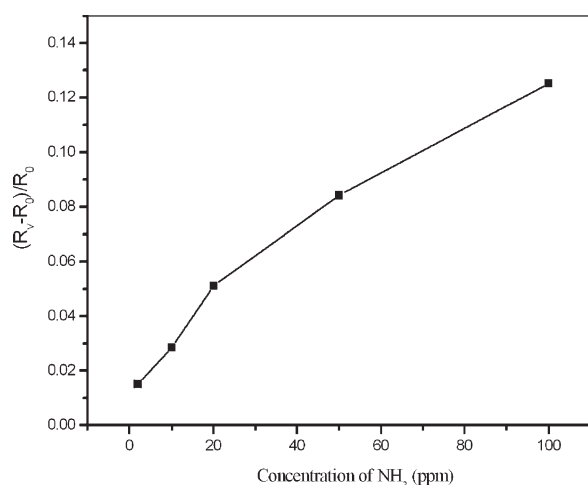


Figure 5 The response of the PPy/TiO₂ composite film to NH₃ at low concentrations.

TABLE II
The Sensitivity of Composite Film with Different Polymerization Condition

Molar ratio of Py to Fe ³⁺	Content of TiO ₂ in composite	Sensitivity (200 ppm NH ₃)
0.5	20%	0.07
1	0	0.07
1	10%	0.1
1	20%	0.16
1	30%	0.11
2	20%	0.14

oxidized or peroxidized below and beyond 1, which both caused the lower sensitivity.

We also investigated the effect of thickness on the sensitivity. The response of the composite films with different thickness is shown in Figure 6. The sensitivity decreases with the increase of the film thickness when other experimental conditions are fixed.²⁴ Hwang et al. developed a simple model based on Langmuir isotherm.²⁵ In this model, the resistance of the composite film can be regarded as the paralleling of several pseudo-monolayers, and each layer is composed of several resistors in series, R , r , n , and m represent resistance of a monolayer, resistance of an active site, thickness of the thin film and the number of active site on a pseudo-monolayer, respectively. By Combining the Langmuir isotherm, they give the expression of sensing response

$$\Delta R_t = (r_1 - r_0) \frac{m}{n} \frac{K_m C_0}{1 + K_m C_0} \quad (2)$$

where K_m is the adsorption equilibrium constant, r_0 is the vacant site resistance, r_1 is the occupied site resistance and C_0 is the concentration. From this formula, we can see that the resistance change (ΔR_t)

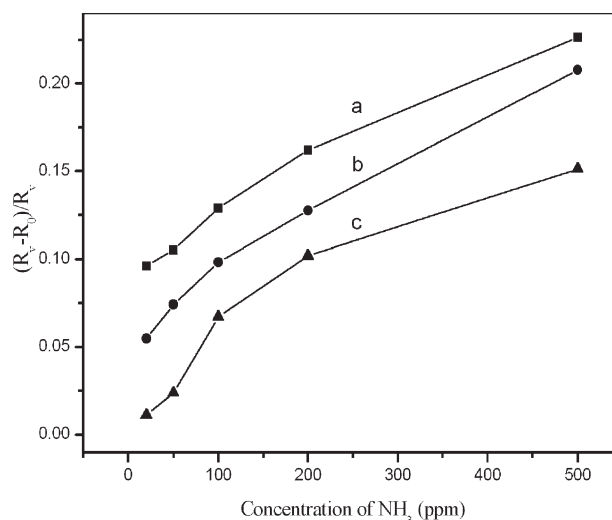


Figure 6 The sensitivities of the PPy/TiO₂ films with different thickness (a) 97, (b) 220, and (c) 248 nm.

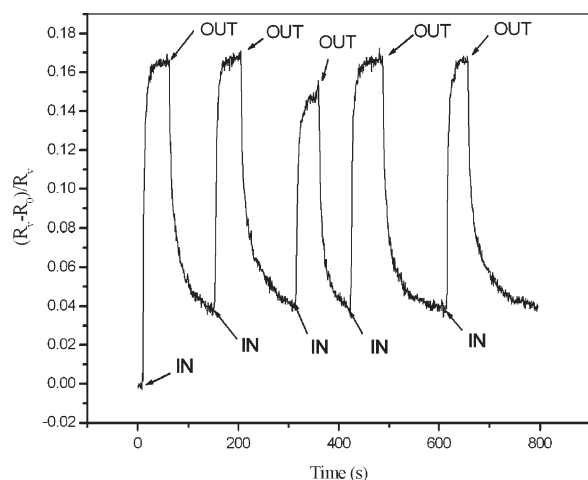


Figure 7 The recover property of the PPy/TiO₂ composite film to 200 ppm NH₃.

was inversely proportional to the thickness of the thin film (n). Therefore, increase thickness showed a decrease of sensitivity.

The PPy/TiO₂ composite film undergoes five on-off cycles by switching between air and 200 ppm of NH₃ to investigate the recover property of the film. As shown in Figure 7, the composite film responses perfectly, recovered properly. The Figure 8 shows the good stability of the composite film in a week.

We have also measured the sensitivity of the composite film to NO₂ gas, and the result is shown in Figure 9. In this figure, when the composite was exposed to acid gas NO₂, the resistance was decreased rapidly because the gas acting as electron acceptors removes the electrons from the p-type conducting polymer composite. The resistance was recovered to the original value when the gas out. The response sensitivity and recovery sensitivity of the composite film to NO₂ were excellent. The

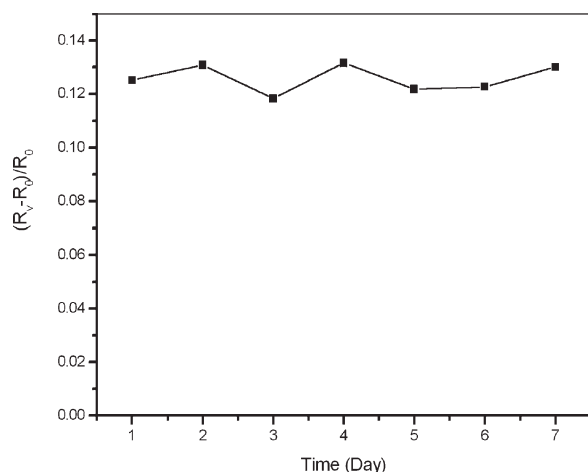


Figure 8 The long-term stability of PPy/TiO₂ composite film to 100 ppm NH₃ in a week.

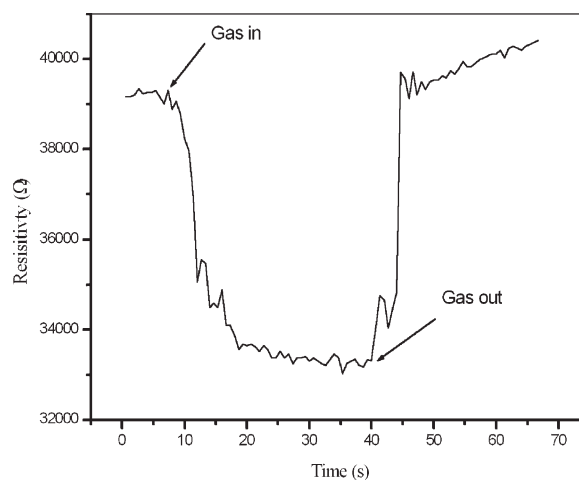


Figure 9 The response of PPy/TiO₂ composite film to 100 ppm NO₂.

research on the NO₂ sensitivity is still under way in our laboratory.

CONCLUSIONS

In this article, we reported the preparation PPy/TiO₂ composite film by *in situ* polymerization process. The films with various thicknesses could be obtained by controlling the polymerization time. It was found that the addition of TiO₂ particles into the PPy structure could improve the corresponding sensitivity to NH₃. The composite film exhibited a very low detection limit of 2 ppm, and the response decreased with increasing the thickness of films. These results showed that TiO₂ could be used to enhance the properties of conducting polymer used in gas sensor.

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