Polymer Bulletin

Examining the use of Fe_3O_4 nanoparticles to enhance the NH_3 sensitivity of polypyrrole films

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Summary

Polypyrrole (PPy) composite films with different contents of Fe_3O_4 were prepared by in-situ polymerization of pyrrole in aqueous solutions. The dependence of dc current changes on the response of the samples exposure to NH_3 vapor has been investigated. The results shows the composite films are more stable than the pristine ones after being exposed to NH_3 vapor. Meanwhile, the response time was reduced with increasing the Fe_3O_4 content in the films. The results might be originated from the structural changes in the PPy films caused by the addition of Fe_3O_4.

1. Introduction

At present, conducting polymers have shown promising applications in gas sensors and they have received extensively attention on detecting and controlling the toxic gases for environment protection [1-3]. Among the conducting polymers, polypyrrole (PPy) has been well studied owing to its excellent conductivity, high yield in redox process, gas sensing ability, response to a wide range of volatile organic compounds and good environment stability [4-7]. In recent years, a lot of investigations of sensitivity to gases have been carried out [8-10]. The conductance of a PPy layer was decreased in the ammonia ambient [11]. The explanation of this behavior was based on traditional solid state concepts. PPy conduction being of p-type, the electron-supplying gases (e.g. ammonia) reduce the charge carrier concentration of the polymer. Thus, on standing in ammonia ambient, the conductance of the PPy film drops. The PPy sensor has demonstrated good sensitivity of the response to ammonia in the range 100-10000 ppm, but in many experiments, the concentration dependence of the response was essentially non-linear. Its response time, however, was rather long and its response was irreversible.

To prepare the optimized properties materials, organic–inorganic sensing hybrid is a widely known technique to obtain new material with complementary behaviors between organic and inorganic materials [12]. For example, Geng et al. reported that the PPy/ SnO_2 composite had sensitivity to organic vapors at room temperature [13]. These types of hybrid materials have shown to possess small grain size and high stability in air. Nardis et al. reported that cobalt porphyrin/ SnO_2 had superior

selectivity to methanol vapor than to CO [14]. On the other hand, Fe_3O_4 as a magnetic oxide has attracted considerable attention as their magnetization, a few literatures refers to the contribution of Fe_3O_4 in nanocomposite on humidity and gas sensitivity. R.P. Tandon et al. investigated the gas sensitivity of PPy/ Fe_3O_4 composites to CO_2, O_2 and N_2, but they did not study the Fe_3O_4 as filler to affect the sensitivity of PPy [15]. The addition of Fe_3O_4 to PPy as filler can create amorphous, flexible regions in polymer and increase the segmental chain mobility of polymer-based sensor, therefore, the transport of vapor will be increased and the sensors can reach stability quickly.

In this paper, we prepared PPy/ Fe_3O_4 composite films by in-situ polymerization of pyrrole that was dispersed with various contents of Fe_3O_4 nanoparticles using $FeCl_3$ as oxidant. The sensing behavior of the films to ammonia vapor was investigated using flow system and the characteristics of the composites were also investigated by SEM, XRD and TGA measurements. The conductivities of the composite films were surveyed also.

2. Experimental

2.1 Materials

Pyrrole was distilled under reduced pressure prior to use, other reagents were analytical grade and used as received without further purification.

2.2 Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared through a typical chemical precipitation method [15]. 250 ml of distilled water was added into a four-necked round-bottomed flask fitted with a nitrogen inlet and an arrangement. $FeCl_3 \cdot 7H_2O$ and $FeSO_4 \cdot 6H_2O$ were added into the flask with a 2:1 molar ratio at room temperature. The entire solution mixture was well stirred under N_2 for 30 min, and then 50 ml of ammonia aqueous solution (1.5 mol / L) was slowly added in dropwise with vigorous stirring. The reaction was allowed to proceed for 2 h. The resulting precipitates were filtrated and washed with distilled water, ethanol and acetone three times, respectively. The resulting particles were dried at room temperature under reduced pressure for 2 days.

2.3 Preparation of PPy / Fe_3O_4 composite films

PPy / Fe_3O_4 films were prepared by in-situ process. In this process, different contents of Fe_3O_4 nanoparticles were dispersed in 200 ml of aqueous solution containing pyrrole monomer under ultrasonic for 20 min. The acetone cleaned transparency was hung with brass wires and immerged into the above solution vertically. After $FeCl_3$ was added as oxidant, the polymerization was allowed to take place for 4 h with continuous stirring at room temperature. Then the transparency was washed by ethanol, acetone and distilled water thoroughly and dried at room temperature under reduced pressure. The pristine PPy film was fabricated using the same approach in the absence of Fe_3O_4.

2.4 Characterization

The morphology of the composite film was observed with scanning electron microscope (SEM, JEOL FESEM JEM-6700F) with gold coating. The X-rays

diffraction (XRD) pattern of the powders was taken with Cu Kα radiation using Shimadzu XRD-6000. The detector ranged from 10° to 60° at a scanning speed of 10°/min. Thermogravimetry analysis (TGA) measurement was carried out on Pyris 6 Thermogravimetric Analyzer (Perkin-Elmer), the samples that scraped from the film was heated at the rate of 10°C min^{-1} up to 600°C using alumina crucibles under constant N_2 flow to minimize mass increase due to iron oxidation, while allowing the PPy to thermally decompose almost completely. The conductivity of the film was measured by the conventional four-probe technique using SDY-5 and the measurement was carried out at 25°C.

2.5 Sensitivity test

The films were connected in series and a 5.0 V supply voltage was regulated with a d.c. power. The current changes of the sample with time were recorded when the sample was exposed to NH_3 vapor. The relative differential current change across each film in test was calculated using the following equation:

$$S = \Delta I/I\% = (I_0 - I_{Vapor}) / I_0 \qquad\qquad (1)$$

Where $\Delta I/I\%$ is the relative differential current change across the film, I_{Vapor} is the current when the film upon exposure to a certain concentration of vapor and I_0 is the current passing through the film before exposure. Response time was defined as the time needed for a film to attain the maximum relative differential change in current.

The test chamber used in this work was designed as shown in Fig. 1. The chamber consisted of a 958 ml glass flask which was sealed with a rubber bung containing a septum. The chamber was firstly flushed with air for 2 min to remove any contaminants from the flask and also to stabilize the film. A syringe was used to inject the required volume of vapor into the chamber. The current changes across the film were recorded. Finally, the flask was flushed with air to remove the vapor and allow the film returning to its baseline value.
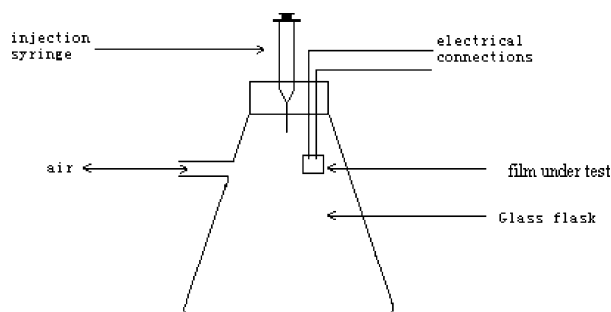

Fig. 1 Schematic representation of the gas sensor test chamber

3. Result and discussion

3.1 SEM

The surface morphologies of the pristine and composite film are shown in Fig. 2. For the micrographs of the polymeric composite films do not show much difference, only the SEM image of the typical PPy / Fe_3O_4 composite film with Fe_3O_4 content of 50 wt% is displayed. From Fig. 2a we can see that the diameter of PPy spherical

particles on pristine film ranges from 70 nm to 200 nm. But the average diameter of spherical particles on composite film is only 20 nm, which can be seen from Fig. 2b. We consider that Fe_3O_4 nanoparticles act as templates to allow pyrrole to be polymerized surrounding the oxide nanoparticles, so the smaller and homogeneity composite nanoparticles are obtained.

In our experiment, the polymerization was taken on the transparency with the major component of polytetrafluoroethylene directly by in-situ method. In this process, pyrrole was adsorbed on the polytetrafluoroethylene transparency due to certain interaction between PPy and polytetrafluoroethylene. Then after the polymerization we could obtain the firm film on the transparency.
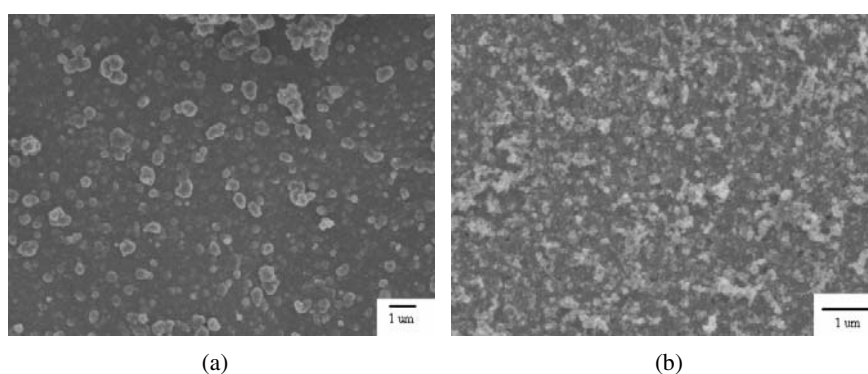

(a)   (b)

Fig. 2 SEM pictures of the PPy film (a) and the typical PPy / Fe_3O_4 composite film (b)

3.2 XRD

Fig. 3 shows the XRD pattern of the PPy / Fe_3O_4 composite.The diffraction peaks of the magnetic composite are measured with 2θ values of 30.10°, 35.50°, 43.12°, 53.44° and 56.96°, respectively. These data are in good agreement with those of Fe_3O_4 [16] and the weak peak at about $2\theta = 25°$ is the symbol of typical amorphous PPy.
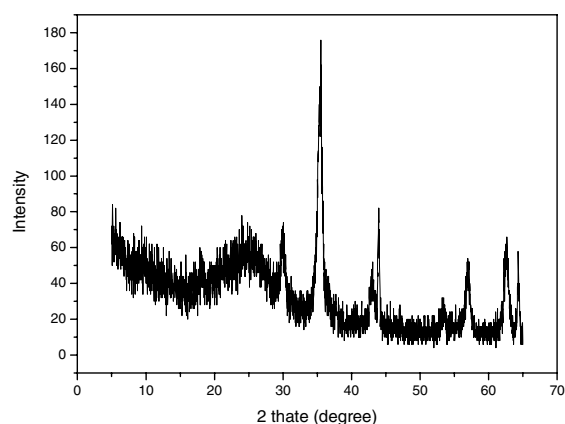

Fig. 3 XRD patterns of the typical PPy/Fe_3O_4 composite film

3.3 TGA

The TGA results of the powder scraped from the composite films with different contents of Fe_3O_4 nanoparticles are shown in Fig.4. From Fig.4, we can see that the weight loss from 50 to 510°C is due to the degradation of PPy. The Fe_3O_4 nanoparticles were thermally stable up to 600°C and remnant weight was consistent with the content of Fe_3O_4 nanoparticles in the different composite films.
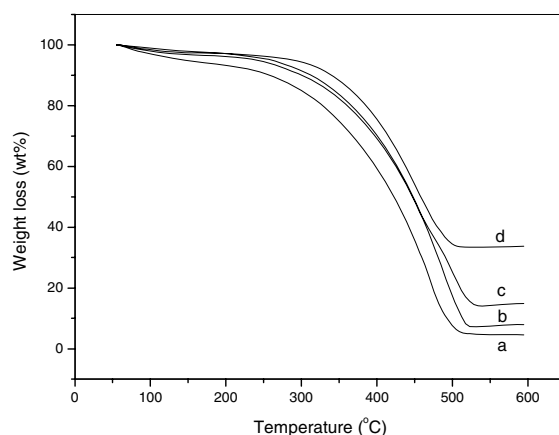

Fig. 4 The TGA curves of PPy/Fe_3O_4 composite with different contents of Fe_3O_4 nanoparticles (a) 13%, (b) 20%, (c) 30% and (d) 50%

3.4 Conductivity

Table 1 gives the conductivity values (S/cm, at room temperature) of the composite films with different contents of Fe_3O_4 nanoparticles. From the Table 1 we can see the conductivity of the pristine film is 1.852 S/cm, but the conductivity value of the composite films decreases with increasing the content of Fe_3O_4 nanoparticles in the film. This may be attributed to increase contents of Fe_3O_4, the relative contents of the conducting polymer PPy decreased. When the content of Fe_3O_4 nanoparticles is increased to 50%, the conductivity is decreased to 0.153 S/cm. This is in agreement with the report of γ-Fe_2O_3-pyrrole system [18].

Table 1 Conductivities of the composite films with different contents of Fe_3O_4 nanoparticles

Content of Fe_3O_4 nanoparticles	Conductivity (S/cm)
13 %	0.709
20 %	0.482
30 %	0.237
50 %	0.153
0	1.852

3.5 Gas sensitivity

Fig. 5 shows the sensitivity of the pristine PPy film and the typical composite film (the content of Fe_3O_4 is 50 wt %) after exposure to 400 ppm NH_3 for 300 seconds to investigate the stability of the films. The results show that the response of the
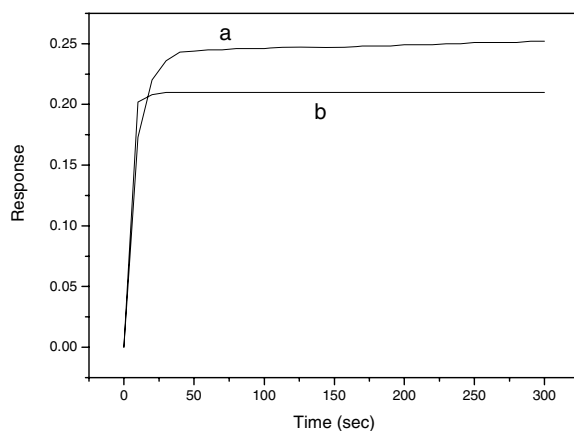
Fig. 5 The response cures pristine PPy (a) and the typical PPy/ Fe_3O_4 composite (b) when exposed to NH_3, the concentration of NH_3 was 400 ppm

composite film increases sharply in the first 20 s and then reaches a steady state in a short time. However, 40 s is required for the response of pristine PPy film and the response increase continuously and slowly after the rapid change.

The dependence of the response time of the films to 400ppm of NH_3 vapor on the content of Fe_3O_4 in the composite is shown in Fig. 6. The response time of the composite film with 13 wt% of Fe_3O_4 is about 240 s .When the content of Fe_3O_4 is increased to 20%, the response time is rapidly decreased 80 s rapidly. With the increasing of the content of Fe_3O_4 subsequent, the response time decreases accordingly. The response time is only 20 s when the content of Fe_3O_4 achieves to 50 wt%, and the film is not uniform beyond 50 wt% content of Fe_3O_4.

The response of the films to vapor can be explained using percolation theory [19]. PPy conduction being of p-type, when the films are exposed to NH_3 vapor, the electron-supplying vapor permeates into the polymer and expands. The expansion of NH_3 in
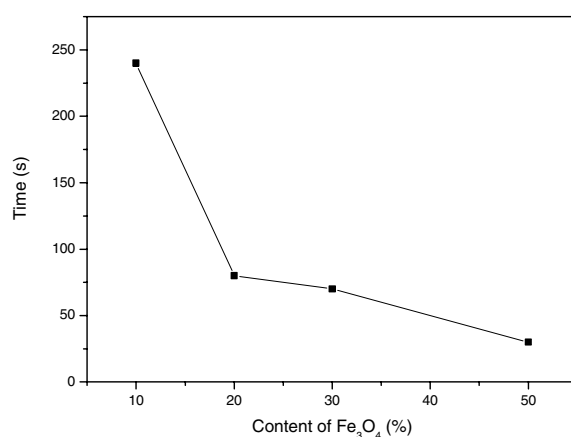

Fig. 6 The response cures for composite film vs. the content of Fe_3O_4 the concentration of NH_3 was 400 ppm
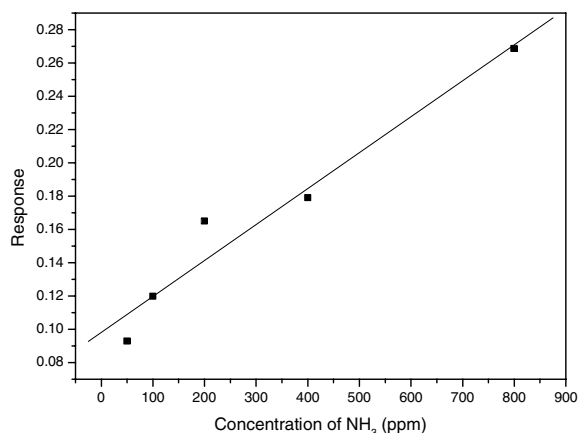
Fig. 7 The maximum relative differential response of the typical composite film to NH$_3$ vapouer at concentrations ranging from 0 to 800 ppm

the PPy reduces the volume fraction of the conducting particles in the film and hence reduces the number of conducting pathways for charge carriers. As a result, the electrical resistance of the composite film rises, and consequently, the current crossing the film decreases. In this process, Fe$_3$O$_4$ nanoparticles create amorphous, flexible regions in PPy and increase the segmental chain mobility of PPy film. Because high segmental chain mobility of the PPy is an important requirement for good absorption of vapor, the improvement of sensitivity is then expected.

Fig. 7 shows the correlation of the maximum relative differential response of the typical composite film versus NH$_3$ vapor concentration ranging from 0 to 800 ppm. The maximum relative differential response increases with the NH$_3$ vapor concentration, and the result shows a good linearity. This illustrates that these results may offer some valuable information for quantitative analysis.

The typical PPy/Fe$_3$O$_4$ composite film undergoes five on-off cycles by switching between air and 400 ppm vapor of NH$_3$ to investigate the reversibility of the film. As shown in Fig. 8, the sensitivity of the composite film keeps constant during the five
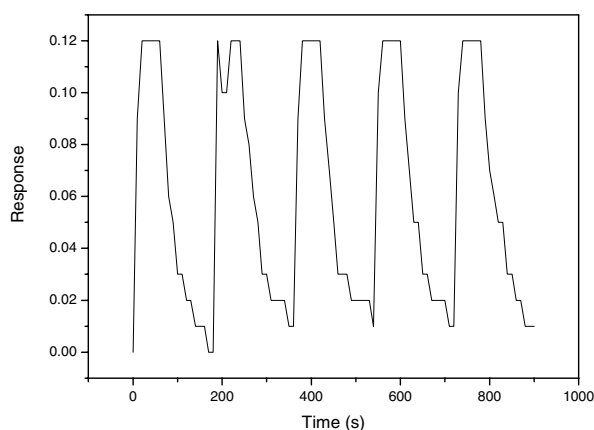

Fig. 8 Dynamic responses of the typical PPy/Fe$_3$O$_4$ films, the concentration of NH$_3$ was 400 ppm

cycles, indicating that the composite film in our experiment has excellent reproducibility and stability.

4. Conclusions

In this work, the sensitivity of pristine PPy film and PPy / Fe_3O_4 composite films to NH_3 was investigated. It was found that the improved sensing stability and reduced response time can be obtained through the addition of Fe_3O_4 particles into the PPy structure. The more weight percentage of Fe_3O_4 nanoparticles in the polymer composite film, the more stable film was. Meanwhile, the response time was reduced with increasing the Fe_3O_4 content in the film. The better stability and shorter response time could be explained by the effect of the oxide particles as filler on the segmental chain mobility of the polymer film. These results showed that iron-oxide could be used to enhance the properties of conducting polymer for gas sensing application.

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