

Porous polypyrrole/polymethylmethacrylate composite film prepared by vapor deposition polymerization of pyrrole and its application for ammonia detection

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Received 8 February 2006; received in revised form 18 December 2006; accepted 4 February 2007

Available online 12 February 2007

Abstract

A simple method has been developed to fabricate porous polypyrrole/polymethyl methacrylate composite films. The synthesis procedures include the vapor deposition polymerization of pyrrole on the composite films of polymethyl methacrylate and ferric hydroxide bis(1,4-bis(2-ethylhexyl) sulfosuccinate), successively, washing the obtained composite films with methanol. Scanning electron microscopic and microscopic Raman spectral studies indicated that the pores had an average size of about 5 μm and they were uniformly dispersed in the whole films. The electrical conductivities of the composite films were measured to be in the range of 10^{-3} to 10^{-2} S cm^{-1} . The porous composite films showed electroactivity, and the sensors based on them exhibited high sensitivity and fast response to ammonia gas.

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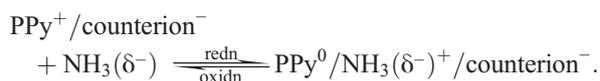
Keywords: Porous composite film; Polypyrrole; Polymethyl methacrylate; Sensor

1. Introduction

Much attention has been paid to polypyrrole (PPy) in the last decades, mainly due to its high electrical conductivity and applications in fabrication of actuators, sensors and electrochromic devices, etc [1–11]. In order to improve the performances of sensing devices, porous conducting polymer films have been prepared because the porous structures provided relatively high active surface areas for detections [12–16]. The porous structures can be prepared by chemical or electrochemical polymerizations *via* template guided growth processes. Up to date, many materials (such as porous films, air bubbles, micro-particles, metal grids, polymer matrix and so on) have been used as the templates [12–21]. Furthermore, the composite films of PPy and other polymers also have been prepared to improve the mechanical properties of PPy [20–24].

On the other hand, the detection of NH_3 gas is an important task in many technological fields, such as industrial processes,

clinical diagnosis, environmental monitoring. In order to activate the adsorption and desorption of the test gases, the gas sensors fabricated by using metal-oxide films [25–27] usually need high working temperatures (250 to 500 °C). In contrast, conducting polymers such as PPy have high sensitivity towards test gases at near room temperature. In its electrically conductive state, PPy is a p-type semiconductor. When PPy is exposed to the gas of an electron donor, e.g. NH_3 , a redox reaction occurs reversibly as following [28]:



The introduction of NH_3 into PPy will lead to the formation of neutral polymer backbones and decrease the charge-carrier concentration of the polymer. As a result, the conductivity of PPy decreases sharply. Based on this mechanism, the sensors for ammonia detection have been fabricated by using PPy films [29–31] or bi-layer PPy/polymethyl methacrylate (PMMA) composite films [2–4] as the active materials.

Recently, Fe-1,4-bis(2-ethylhexyl) sulfosuccinate (AOT) system has been proved to be a convenient method for

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fabricating nano-structures of PPy and other materials [32–34]. Composite materials with nano-structures also have been prepared by using vapor deposition polymerization and soft template-guided growth techniques [35,36]. In this paper, we desire to describe a simple method for preparing porous PPy/PMMA composite films by reacting pyrrole vapor with an organic ferric salt embedded in PMMA films. The ammonia sensors based on these composites were tested to have relatively high sensitivity and fast response.

2. Experimental section

2.1. Chemicals

Pyrrole was purchased from the Chinese Army Medical Institute (Beijing, China) and distilled under reduced pressure prior to use. Sodium 1,4-bis(2-ethylhexyl) sulfosuccinate was purchased from ACROS and used without further purification. PMMA particles were synthesized by emulsion polymerization according to previous method [37]. And other chemicals were reagent grade and used directly.

2.2. Preparation of the organic ferric salt (FeAOT)

The ferric salt was prepared by reacting 0.03 mol AOT with 0.01 mol ferric chloride in 20 ml distilled water under stirring for 24 h. After the resulted red precipitation was collected and dried under vacuum for 48 h, the rough product was dissolved into about 50 ml chloroform. After filtration, the solvent was removed under reduced pressure. Finally, the product (FeAOT) was dried under vacuum at 50 °C for 48 h. X-ray photoelectron spectroscopy results demonstrated that the atomic ratios of Fe:S:C in FeAOT were 1:2:40. Elemental analyses indicated the product had 48.35% carbon, 8.40% hydrogen and 6.81% sulfur [33]. According to above results, we concluded that FeAOT had a chemical formula of $\text{FeC}_{40}\text{H}_{75}\text{O}_{15}\text{S}_2 \cdot 4\text{H}_2\text{O}$ (FeAOT₂OH·4H₂O) (calculated, C: 48.58%, H: 8.40%, S: 6.47%).

2.3. Preparation of porous PPy/PMMA composite films

Various amounts of FeAOT were dissolved into 25 ml chloroform solution of PMMA (5 mg/ml). The mixtures were cast onto 2.5 cm×3.5 cm glass slides. After drying in air for 12 h, the FeAOT/PMMA films were placed into the pyrrole vapor for 12 h. Then, the films were immersed in methanol repeatedly to wash the resulted Fe²⁺ AOT, and dried under vacuum at room temperature for 24 h. The mass contents (wt.%) of PPy in the composite films were measured to be 3.0, 5.9, 11, 17 and 20%. The thickness of the composite films ranged from 8 to 20 μm, correspondingly.

2.4. Preparation of the electrodes coated with PPy/PMMA

The mixtures (100 μl) of PMMA and various amounts of FeAOT were dropped onto stainless steel sheets (AISI 304) with surface areas of 1 cm×0.5 cm each. After being dried in air, the electrodes were treated with pyrrole vapors for 12 h.

Then the electrodes were washed with methanol and dried under vacuum.

2.5. Fabrication and test of ammonia gas sensors

The composite porous film of PPy/PMMA was cut into small strips with a size of 1.0 cm×0.3 cm each. A strip was adhered to a glass slide (1.0 cm×0.5 cm) with adhesive tape, and two copper electrodes with a distance of 5 mm were contacted to the strip by using two small clamps.

The fabricated gas sensor device was introduced into a test chamber with volume of 500 cm³ and the temperature was stabilized to be 25±1.0 °C. The device was connected to an electrochemical instrument (EG and G Princeton Applied Research, model 283) under computer control. At first, the device was kept to equilibrate for about 1 h in air at 25 °C before test (flow rate: 1.5 L min⁻¹). Appropriate concentrations of ammonia gas were obtained in the test chamber by injecting known volumes of gas via a gas tight syringe. The response to each ammonia vapor was measured for 2 min and then the sensor was purged by using air at a flow rate of 1.5 L min⁻¹.

The percentage of relative change of the sensor resistance was commonly defined as $[\Delta R/R]\% = [(R_{\text{gas}} - R_0)/R_0]\%$, where R_0 was the electrical resistance of the sensor in air, and R_{gas} was the steady value of the electrical resistance after exposing to the test ammonia gas.

2.6. Instruments

The morphology of the composite films was studied by using a KYKY2800 scanning electron microscope (SEM) after sputter-coating the samples with thin layers of gold. It was operated at an accelerating voltage of 25 kV. X-ray photoelectron spectroscopy (XPS) data were recorded by using a PHI 5300 ESCA/610 SAM spectrometer. A monochromatic Al Kα X-ray source with a power of 250 W was used, and the vacuum of the analysis chamber was less than 1.33×10^{-6} Pa. The analyses of C and H were performed on FLASH EA1112 and S on Carlo Erba 1106 elemental analysis instrument. Electrochemical characterizations were performed in one-compartment cell by using an electrochemical instrument (EG and G Princeton Applied Research, model 283) under computer control. A stainless steel (AISI 304) coated with porous PPy/PMMA film (surface area=1 cm×0.5 cm) was used as the working electrode; a naked stainless steel sheet (area=3 cm×2 cm) was used as the counter electrode, and a saturated calomel electrode was employed as the reference electrode, and 1.0 mol L⁻¹ LiClO₄ aqueous solution was used as electrolyte. All solutions were de-aerated by bubbling dry nitrogen, and maintained a light nitrogen overpressure during the experiments. Sensor testing was carried out on the same instrument as electrochemical characterization using a chronopotentiometry mode, and the current was kept in 6×10^{-4} A.

Raman spectra were recorded on an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC., England) by employing a 633 nm laser beam and a charge coupled device

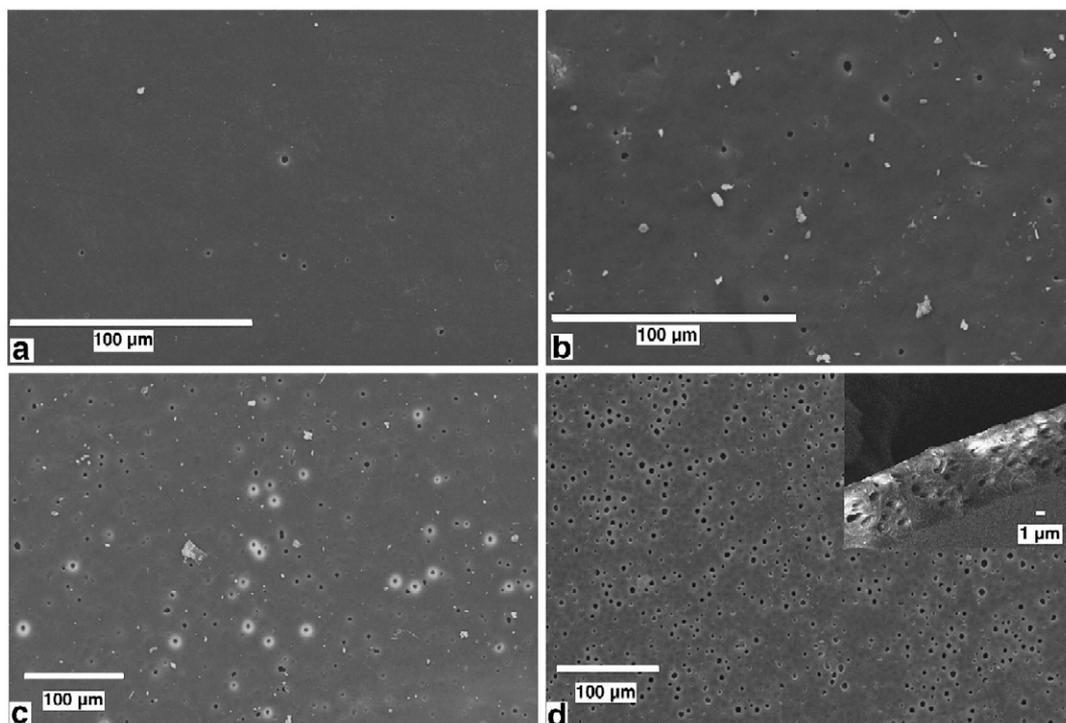


Fig. 1. SEM images of the PPY/PMMA composite films with various weight contents (wt.%) of PPY. a) 3.0%; b) 5.9%; c) 11%; d) 20% (inserted image: cross-section SEM image of the film).

detector with 4-cm^{-1} resolution. The spectra were recorded by using a $20\times$ objective and accumulated for 30 s. The power was always kept very low (~ 0.5 mW) to avoid destroying the samples. The composite membrane was cut vertically into two pieces. The laser light spot was focused on the newly formed cross-section and the spectra of the composite films were recorded. The direct current conductivity was measured by conventional four-probe method.

3. Results and discussions

3.1. Morphology and conductivities

The typical scanning electron microscope (SEM) images of the PPY/PMMA composite films are shown in Fig. 1. It is interesting to find that there are many pores dispersed in the composite films. Moreover, the pores density increases with the increase of PPY content in the films (Fig. 1a–d). The average pore size is measured to be approximately $5\ \mu\text{m}$. From the

inserted cross-section image of the film (Fig. 1d inserted image), we can find that the pores with diameter of several micrometers are dispersed in the film. It should be noted that the composite films were made by casting process, and a phase separation must occur more or less during the process of solvent volatilization. As a result, FeAOT did not disperse in PMMA very uniformly. When the composite films were treated with pyrrole vapor, as-formed PPY aggregated together with PMMA frameworks. After the removal of the formed organic salt Fe^{2+}

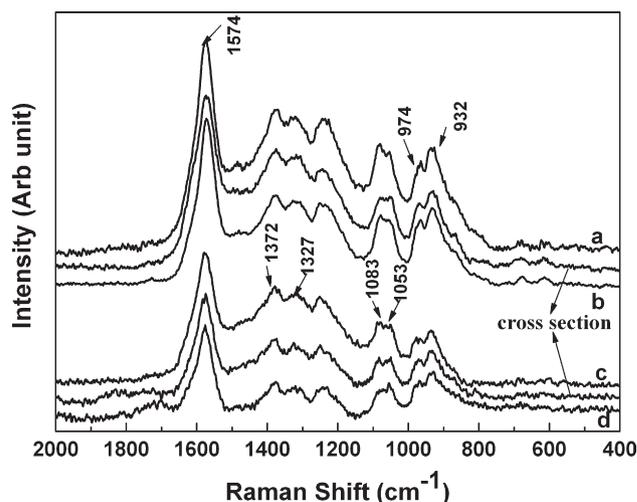


Fig. 2. Raman spectra of the PPY/PMMA composite films containing (wt.%) 20% PPY (a and b) and 3.0% PPY (c and d) and recorded at the surfaces in contact to air (b, c) or at the surfaces in contacted with the glass slides (b, d).

Table 1
The conductivities of the porous PPY/PMMA composite films

PPy content (wt.%)	Conductivities (S cm^{-1})	
	Face in exposed to pyrrole vapor	Face in contact to glass
3.0	2.61×10^{-3}	1.26×10^{-4}
5.9	2.15×10^{-2}	4.13×10^{-3}
11	2.34×10^{-2}	7.20×10^{-3}
17	2.12×10^{-2}	1.36×10^{-2}
20	2.14×10^{-2}	1.33×10^{-2}

AOT from Fe^{3+} AOT by methanol, pores were left in the films (because PPy and PMMA are insoluble in methanol).

The conductivities of the composite films are listed in Table 1. It can be seen clearly from this table that the conductivities of the two sides of the composite films are different, for example, the side exposed to pyrrole vapor has a higher conductivity than that of the side contacted to the glass slice. This result indicates that the content of PPy in the composite film is not spatially uniform. From Table 1, we also can find that the conductivity of the surface exposed to pyrrole vapor increased from 2.61×10^{-3} to 2.34×10^{-2} S cm^{-1} as the content of PPy increases from 3% to 11% (wt.%). However, as PPy content was higher than 11%, the conductivity of the surface exposed to pyrrole did not show apparent change. This is possibly due to the increase of PPy content that resulted in the increase of pores density, and also

the increase of film thickness (from 8 μm for 3% PPy content to 20 μm for 20% PPy content). These two factors partly counteracted the increase of conductivity caused by the increase of PPy content.

3.2. Raman spectra and electrochemical properties

In order to monitor the changes of PPy component in the films, a composite film is cut vertically into two pieces and the laser light spot is focused on the newly formed cross-section to record the Raman spectra. Fig. 2 illustrates the Raman spectra of the PPy/PMMA composite films in which different amounts of PPy are contained. We can find that all the Raman spectra of the composite films are similar to that of pure PPy prepared from electrochemical polymerization [38]. The strong band located at ca. 1574 cm^{-1} represents the C=C backbone stretching of PPy.

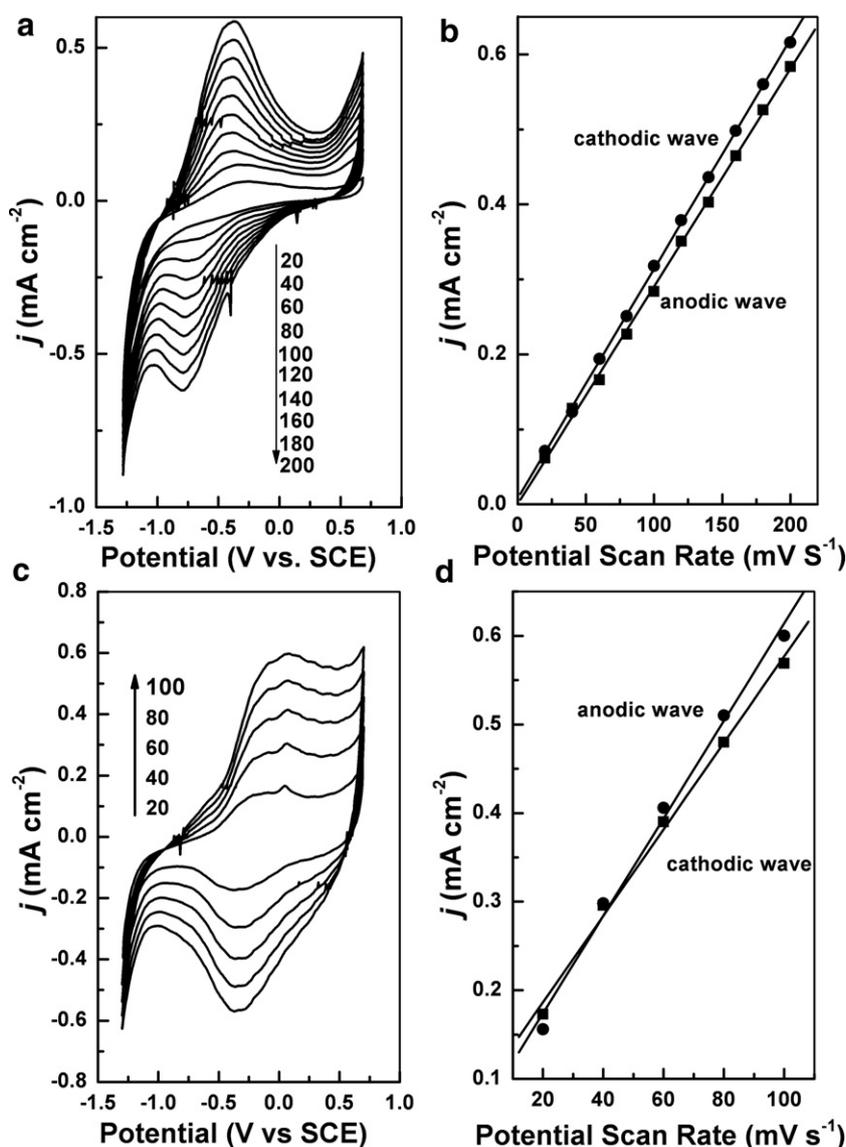


Fig. 3. Cyclic voltammograms of a PPy/PMMA composite film deposited on a stainless steel electrode at various potential scan rates in 1.0 mol L^{-1} aqueous solution of LiClO_4 . (a) PPy content=3.0% (wt.%), potential scan rate range=20–200 mV s^{-1} ; (b) plots of wave current density versus potential scan rate for a; (c) PPy content=20% (wt.%), potential scan rate range=20–100 mV s^{-1} ; (d) plots of wave current density versus potential scan rate for c.

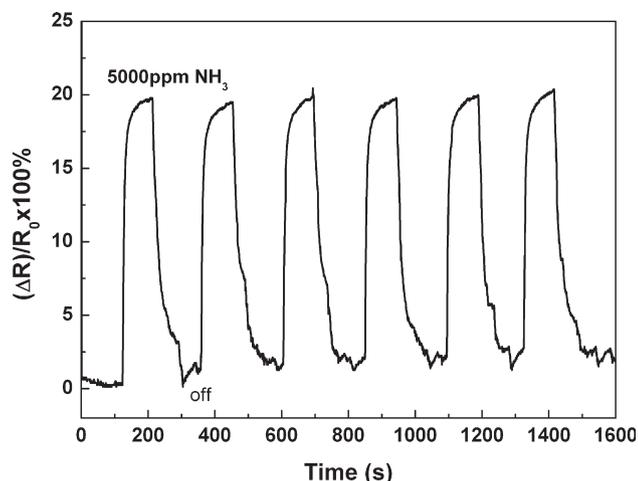


Fig. 4. The resistance response of the gas sensor based on a PPy/PMMA (20% PPy in wt.%) composite film towards 100 s ammonia gas pulses (5000 ppm in air at room temperature) versus time at 25 °C.

The double peaks at about 1053 and 1083 cm^{-1} are assigned to the C–H in plane deformation. The other double peaks at ca. 1327 and 1372 cm^{-1} are attributed to the ring-stretching mode [39–41] of PPy. And the bands located at about 932 and 974 cm^{-1} are assigned to the ring deformations associated with dication (bipolaron) and radical cation (polaron), respectively. From this figure, we can also find that the Raman spectra recorded from the surfaces are almost the same as that recorded from the cross-section (the spectra in different places of the cross-section are very similar). These results reveal that PPy exists in all the parts of the composite films. Unfortunately, we can't determine the precise content of PPy in different parts of the composite films.

The electrochemical activity of a PPy/PMMA composite film coated on a stainless steel electrode is studied in 1.0 mol L^{-1} aqueous solution of LiClO_4 . As shown in Fig. 4, the cyclic voltammograms of the PPy films have a couple of broad oxidation and reduction waves and the films have good electrochemical stability. The wave currents have linear relationships with potential scan rates range 20–200 mV s^{-1} (3.0 wt.% PPy content) and 20–100 mV s^{-1} (20 wt.% PPy content) for composite films (Fig. 3). These results indicate that the mass and electron transfers are fixed on the electrodes (Fig. 4). Furthermore, the films can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) state without significant decomposition. The pure PPy doped with AOT anion films coated on a metallic (unstained steel) electrode shows a reduction wave at ca. -0.67 V and an oxidation wave at ca. -0.11 V [38], the value of $E_{1/2}$ ($E_{1/2} = (E_{\text{anodic}} + E_{\text{cathodic}})/2$) is -0.39 V. On the other hand, the composite films show different reduction and oxidation waves in contrast to those of pure PPy. For example, the composite films with 3.0% PPy content show an $E_{1/2}$ of about -0.56 V, which is more negative than that of the pure PPy. This result reveals that the electrochemical properties of PPy can be influenced by PMMA matrix in which PPy is dispersed, because the conductivity of the composite films depends strongly on its PMMA content.

3.3. Electrical conductivity response toward ammonia gas

Fig. 4 shows the real-time responses of ammonia sensor prepared from PPy/PMMA composite films containing 20% PPy. After exposing to 5000 ppm ammonia gas, the electrical conductivity of the sensor decreased dramatically. It took about 120 s for the response of the sensor to reach the maximum. Furthermore, the response quickly recovered to the baseline as the ammonia gas was turned off. This response time is shorter than those of other ammonia detectors [2–4]. The total time of a gas on/off cycle is about 250 s. And six gas on/off cycles produced similar responses, indicating the repeatable detection properties of the composite films.

Fig. 5a demonstrates the electronic resistance response of the composite films towards 30–850 ppm ammonia gas concentration. The detectable limit of this device is about 30 ppm, which is close to that of Langmuir–Blodgett (L–B) polypyrrole film devices (46 ppm) [3]. Fig. 5b shows the calibration curve of the sensor in the ammonia concentration

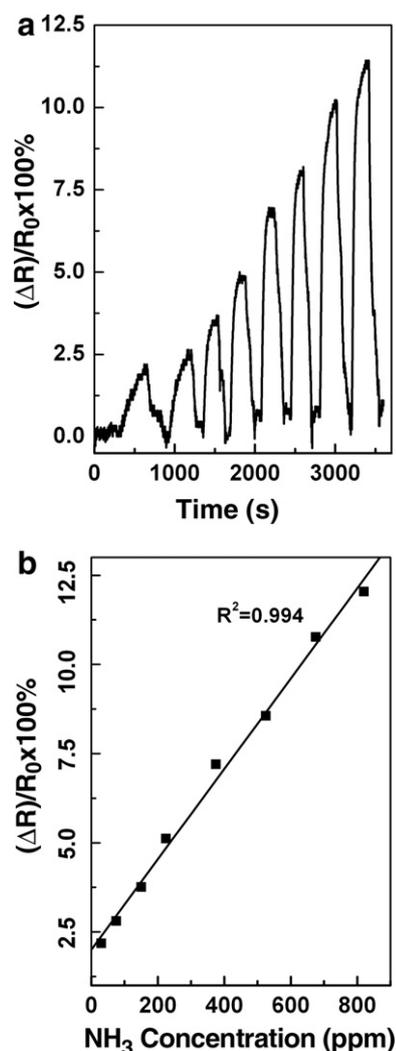


Fig. 5. The resistance response of the composite film versus various concentration of NH_3 (a) and the plot of resistance increase percentage versus NH_3 concentration (b) at 25 °C.

within the range of 30–850 ppm in air. This curve is linear and its slope is as high as 0.01267%/ppm. This value is two times higher than that of the sensor based on electrochemical deposited PPy films [42] and close to that of the sensor based on L–B PPy films (0.01275%/ppm) [2]. This is mainly due to the porous PPy/PMMA film that has a larger active specific surface area than that of an electropolymerized PPy film.

4. Conclusions

A convenient method has been developed for preparation of porous PPy/PMMA composite films by treating FeAOT/PMMA composite film with pyrrole vapors. The films have a high pore density and their pore sizes are almost uniform. A simple resistance device based on this composite film has been fabricated and applied to detect ammonia gas at room temperature. The sensitivity of the porous composite films towards ammonia is considerably higher than that of an electrochemically deposited PPy films. Furthermore, the response speed of the sensors is also fast. And the porous films have better reproducibility towards ammonia than that of the electropolymerized and L–B PPy films. The results suggest that the porous PPy/PMMA composite films are one of the optima for fabricating sensitive and low-cost ammonia sensors.

Acknowledgement

This work was supported by National Natural Science Foundation of China with grant numbers of 20604014, 50225311, 20374034, 50533030 and 973 project with grant no.2003CB615700.

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