

Sensing characteristics of polypyrrole–poly(vinyl alcohol) methanol sensors prepared by in situ vapor state polymerization

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Abstract

Polypyrrole (PPy)–poly(vinyl alcohol) (PVA) composite and pure polypyrrole methanol sensors were prepared by an in situ vapor state polymerization method and their chemical structures were identified by a FT-Raman spectroscopy. The various electrical sensing behaviors of both types of sensors were systematically investigated by a flow measuring system including mass flow controller (MFC) and bubbling bottle. The incorporation of PVA into the polymer film caused a higher sensitivity than that of pure PPy sensor, while the response and recovery time and long-term stability were worse. The effect of thickness of sensing film was also investigated, and it was found that the thinner film showed higher sensitivity, which indicated that the resistance involved in sensing behavior comes from bulk resistance of sensor rather than surface resistance.

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1. Introduction

Conducting polymers have attracted much interest as novel materials for potential applications in actuators, chemical and biosensors, capacitors, catalyst and electronic devices [1–8]. The most commonly applied polymers for gas sensing applications have been those based on polypyrrole (PPy), polyaniline (PAN), polythiophene (PTP) and their derivatives [9]. Among those conducting polymers, PPy has been extensively studied owing to its excellent conductivity, high yield in redox process, gas sensing ability, optimum performance at room temperature, response to a wide range of volatile organic compounds (VOCs) and environmental stability [9–12].

Polypyrrole can be prepared in three ways. In 1968, Bocchi and co-workers initially deposited PPy by electrochemical polymerization, which was carried out in dilute sulfuric acid [13]. Diaz et al. synthesized the first free-standing PPy films electrochemically in 1979 [14]. Bartlett et al. proposed to electrochemically deposit PPy in the development

of gas sensor [2]. Generally, it has been well known that PPy films can be synthesized by either an oxidative chemical or electrochemical polymerization of pyrrole in a liquid phase with existence of oxidizing agent, normally, copper(II), silver(I) and iron(III) [15,16]. In general, PPy polymerized either electrochemically or chemically is known to be insoluble due to the strong inter- and intra-molecular interactions and crosslinking [17]. The insolubility of PPy gives rise to processing difficulties and thus has limited its applications. However, PPy composite can be prepared by a rather easy and laborious fabrication process, i.e. vapor state polymerization [18–20]. The vapor state deposition was normally carried out by exposing an initiator containing activated substrate to pyrrole monomer. This method resolves the problem of insolubility of PPy, and hence improves its processibility.

The major problems with PPy are its very fragile structure and poor adhesion to electrode. Attempts to overcome these have been centered on incorporating PPy within the matrix of other supporting materials. Many kinds of supporting substrates for chemical polymerization of polypyrrole have been used, e.g. PVC [21], PTFE [22], PAI [23] and PMMA [24]. Poly(vinyl alcohol) (PVA) possesses the advantages including its flexible molecular chains, good adhesion to elec-

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trodes and its ductile nature and therefore, is a desirable material to be incorporated with PPy. There are several ways to prepare PPy/PVA composite. In 1984, Lindsey and Street proposed electrochemical blending of PPy/PVA composite [25]. In 1986, Ojio and Miyata prepared highly transparent and electrically conducting PPy/PVA composite film by gas state polymerization [18]. Recently, Lin et al. conducted electrochemical co-polymerization of pyrrole with PVA dispersion [26].

In this work, we investigated the sensing characteristics of electrically conducting PPy/PVA polymer composite and pure PPy gas sensors prepared by a continuous vapor state polymerization process. The structure identification of vapor state polymerized PPy was carried out by FT-Raman spectroscopy. The systematic study of sensing characteristics of the sensors were reported herein, including dynamic response to target gas, response time and recovery time, reproducibility, and long-term stability. The effects of the existence of PVA and the thickness of sensing film on the sensing behaviors were also investigated.

2. Experimental

Poly(vinyl alcohol) ($M_n = 30,000\text{--}70,000$, Sigma) and ferric chloride (anhydrous, Aldrich) were used as supplied. Pyrrole (Aldrich) was distilled before use and stored in a freezer maintained at 0°C . A 4% PVA incorporated with FeCl_3 , [PVA]:[FeCl_3] ratio of 1:3, was diluted by de-ionized water. This solution was then spin-coated onto an interdigitated Pt/Pd alloy electrode (the schematic diagram of the electrode was shown in Fig. 1) and dried in oven at 70°C for 10 min under atmosphere pressure. The polymerization was carried out in a vaporization chamber under N_2 condition, by exposing the pre-coated electrode to distilled pyrrole and H_2O vapors at 10°C for 1 h. The polymer composite thus prepared was a uniform and dark thin film. Following the polymerization, the electrode covered by conduc-

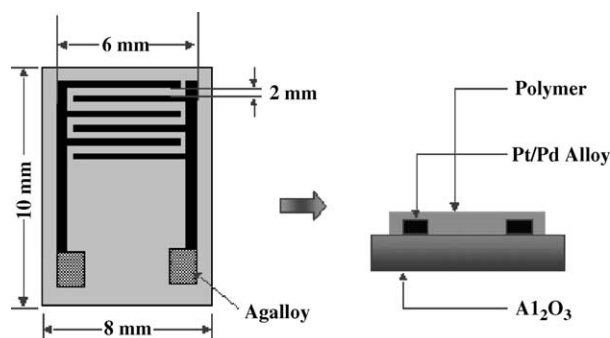


Fig. 1. Schematic diagram of the interdigitated electrode.

ing polymer was soaked at room temperature in ethanol for 12 h to remove pyrrole monomer, unreacted FeCl_3 and other contaminants. Finally, the sensor was dried again at 70°C for 10 min. To probe the effect of the existence of PVA on the sensing behaviors, pure PPy sensors were also prepared by vapor state polymerization. The preparation procedure was almost the same with that of PPy/PVA composite, except that the FeCl_3 containing matrix PVA solution was replaced by aqueous FeCl_3 solution. Chemical structure identification was investigated by FT-Raman spectroscopy. The sensing characteristics investigation was carried out by using a volatile organic compounds (VOCs) sampling system (shown in Fig. 2) at 25°C .

3. Results and discussion

The FT-Raman spectroscopy was used to identify the molecule structures of polypyrrole prepared by vapor state polymerization. It was generally known that the vibrational spectra provide information on the chemical structure of polymer, and can help investigate the state of conjugation of polymer [27,28]. From Fig. 3, we can see that the FT-Raman spectroscopy of the vapor state polymerized PPy/PVA, pure

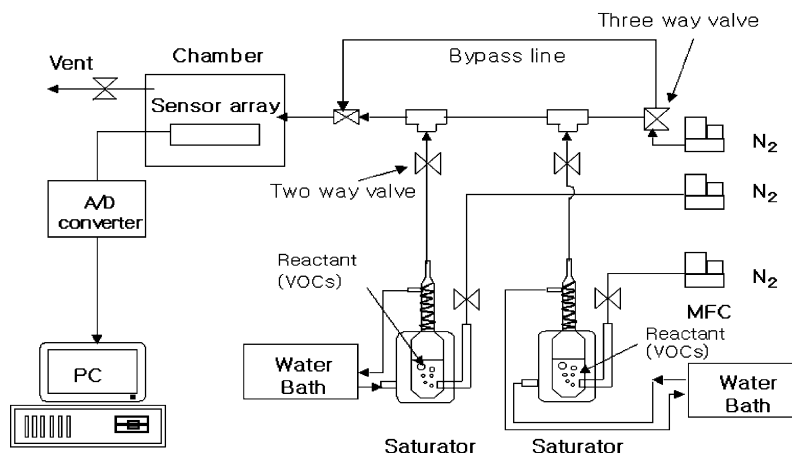


Fig. 2. Schematic diagram of VOCs sampling system for measuring the electrical properties of sensor.

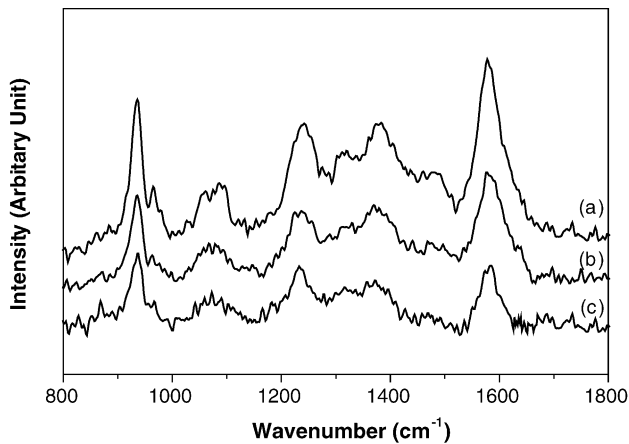


Fig. 3. FT-Raman spectroscopy of (a) chemically polymerized PPy, (b) vapor-phase polymerized PPy and (c) vapor-phase polymerized PPy/PVA composite.

PPy and chemically polymerized PPy were identical to each other, confirming the same molecule structure. However, the PVA-related peaks did not appear in the spectroscopy because the amount of PVA in the substrate-oxidant solution was very small.

The FE-SEM morphologies of two types polymer sensors were investigated and shown in Fig. 4. PPy/PVA composite sensor is more dense than pure PPy. In addition, some cracks were observed in the pure PPy sensor, which was thought to occur during heat treatment at 70 °C for 10 min. This phenomenon, however, was not observed in the PPy/PVA composite sensor.

The concentration of methanol gas was calculated according to the equation:

$$C = \frac{(P^* \times L)/760}{((P^* \times L)/760) + L + L^*} \times 10^6$$

where L and L^* are the bubbler gas flow rate and dilute gas flow rate (sccm), respectively, and P^* is the vapor pressure of methanol gas (mmHg), calculated according to

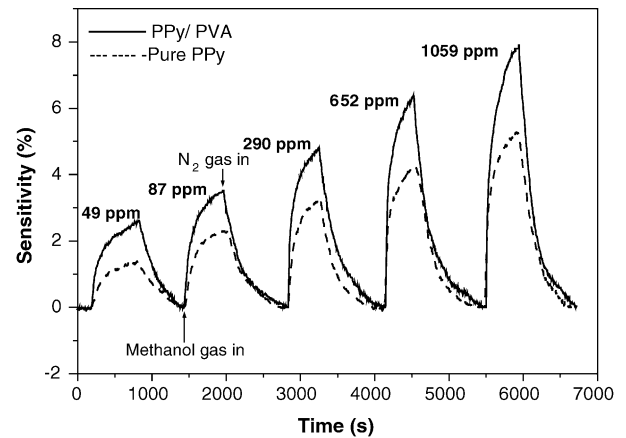


Fig. 5. Dynamic responses of PPy/PVA composite sensor and pure PPy sensor upon exposure to methanol gas.

Antoine equation:

$$\log P^* = A - \frac{B}{T + C} P^*$$

where A , B , and C are the constants for a certain type of gas and T is the temperature in °C. Sensitivity is defined as

$$S (\%) = \left(\frac{R - R_0}{R_0} \right) \times 100$$

where R_0 and R are the initial resistance of sensor in air and in target gas, respectively.

Fig. 5 showed the dynamic responses of PPy/PVA composite sensor and pure PPy sensor upon exposure to methanol gas in the range of 49–1059 ppm. According to conventional semiconductor theory [29], polypyrrole is a p-type semiconductor, the exposure to electron-donating gases, such as alcohol gases, will cause an increase in the resistance. This was in good agreement with our experiment results. The sensitivity of PPy/PVA sensor upon exposure to 49 ppm methanol gas was 2.6%. The initial resistance of sensor was on the order of magnitude of $\sim 30 \text{ k}\Omega$, and the sensitivity of 2.6% indicated that the resistance change

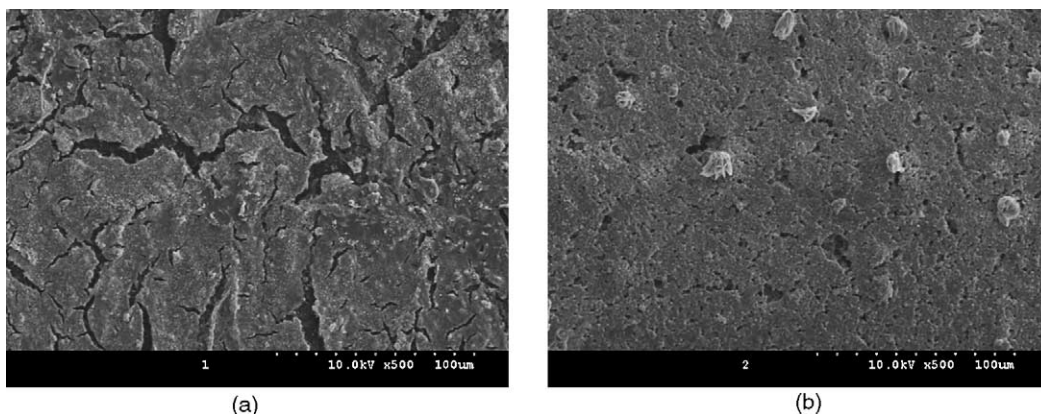


Fig. 4. FE-SEM morphologies of (a) pure PPy sensor and (b) PPy/PVA composite sensor.

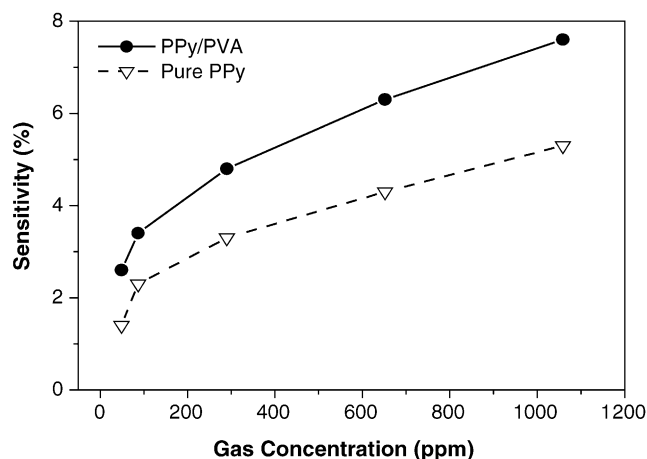


Fig. 6. Variation of sensitivity with gas concentration of PPy/PVA composite and pure PPy.

was about $1\text{ k}\Omega$, which was much larger than previous reported figures of sensors prepared by electrochemical polymerization [26]. The comparison of the sensitivity of PPy/PVA composite sensor and pure PPy sensor was shown in Fig. 6. Both types of sensors showed linear relationship between sensitivity and gas concentration in the gas range of 50–1059 ppm. The PPy/PVA composite sensor had a higher sensitivity in all range of gas concentrations than that of pure PPy sensor, the reason of which still need further study and investigation.

We define abruptly the response and recovery time as the time of 90% total resistance change. The response and recovery times of pure PPy and PPy/PVA composite sensors were tabulated in Table 1. We can see that the response times of both types of sensors are about 5 min, which are a little longer than that of sensors prepared by electrochemical polymerization [26], even though direct comparison was difficult. In addition, the response times and recovery did not change even when the sensors were exposed to the high concentration of methanol gas, indicating that there is no much dependence of response and recovery time on gas concentration. The response and recovery times of PPy/PVA composite sensors were longer than those of pure PPy sensors. It can be explained from the fact that, as suggested by other researchers [26], the methanol molecules permeated

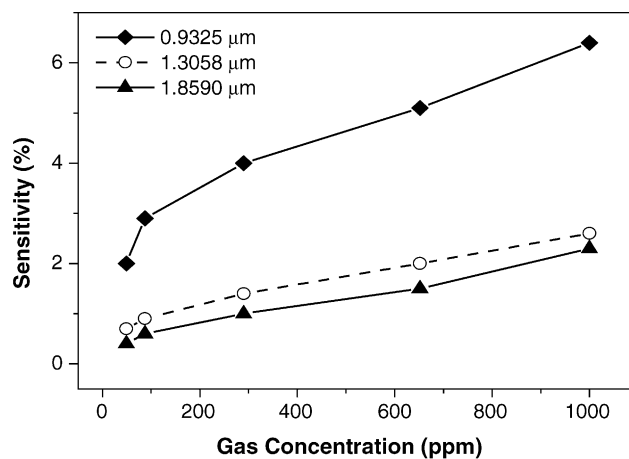


Fig. 7. Variation of sensitivity with gas concentration of PPy/PVA composite with different thickness.

into polymer composite formed a strong bonding with the hydrophilic groups on PVA chains and gave rise to slower adsorption and desorption rates which consequently resulted in longer response and recovery time. In all cases, the recovery time was always longer than the response time.

We also investigated the effect of thickness of sensing film on the sensitivity of sensor. The comparison of sensitivities of sensors with different thickness was shown in Fig. 7. The three sensors were pretreated by spin-coating PVA– FeCl_3 solution onto electrodes for one to three layers, respectively. The subsequent preparation procedures were as stated in Section 2. Fig. 7 clearly showed that the sensitivity decreased with the increase of the thickness of the sensing film when other experimental condition was fixed. As shown in Fig. 4, the surface of PPy/PVA composite sensor was very dense, which could prevent gas molecules from penetrating into the bulk. If only gas molecules adsorbed on surface of film contribute on the sensitivity of sensor, it was thought that the change of resistance in thinner film was larger than that of thicker film, exposed to target gas, even though the same amounts of gas molecules were adsorbed on the surface of all sensors. In addition, this indicates that the resistance of sensor involved in the sensing process was bulk resistance rather than surface resistance of sensor.

The PPy/PVA composite sensor underwent eight on–off cycles by switching between N_2 gas and 3000 ppm methanol gas. As was shown in Fig. 8, the sensitivity of sensor kept constant during the eight cycles which thus indicated that the reproducibility of our sensor was excellent. In the first test, the sensing curve did not completely recover back to baseline when methanol gas was switched off. However, this phenomenon did not occur any longer in the subsequent cycles. PPy/PVA composite sensor having dense surface morphology can prevent gas molecules from diffusing into the bulk and gas molecules can be distributed from surface (rich in concentration) to bulk (poor). If any molecules within film were not almost completely desorbed due to the diffu-

Table 1
The response and recovery times of PPy/PVA and pure PPy sensors upon exposure to methanol gas

Gas concentration (ppm)	Response time (s)		Recovery time (s)	
	PPy/PVA	PPy	PPy/PVA	PPy
49	384	374	496	470
87	362	282	470	352
290	334	290	466	358
652	304	298	512	348
1059	316	308	532	392

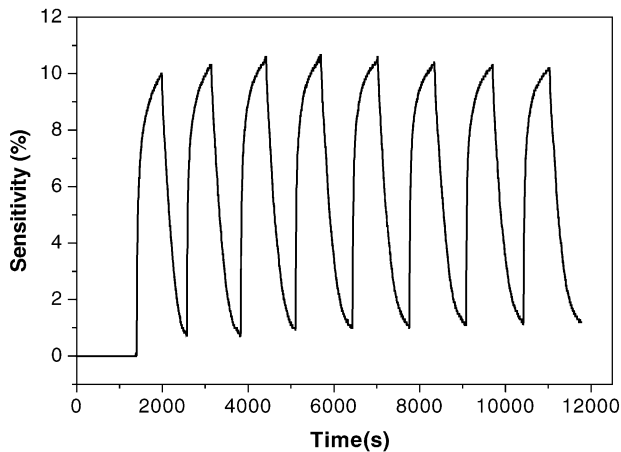


Fig. 8. Reproducibility of PPy/PVA composite sensor upon exposure to 3000 ppm methanol gas.

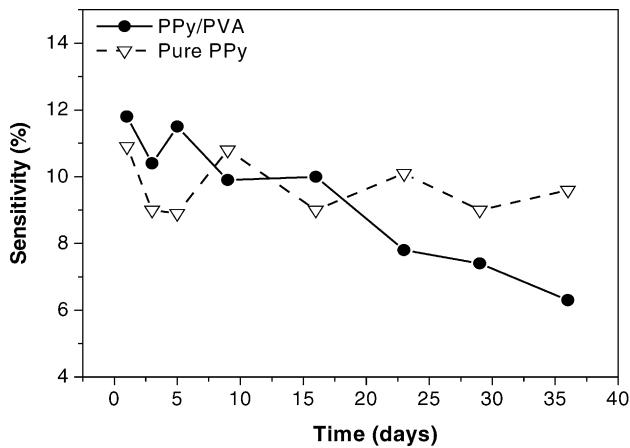


Fig. 9. Long-term stability of PPy/PVA composite and pure PPy sensor.

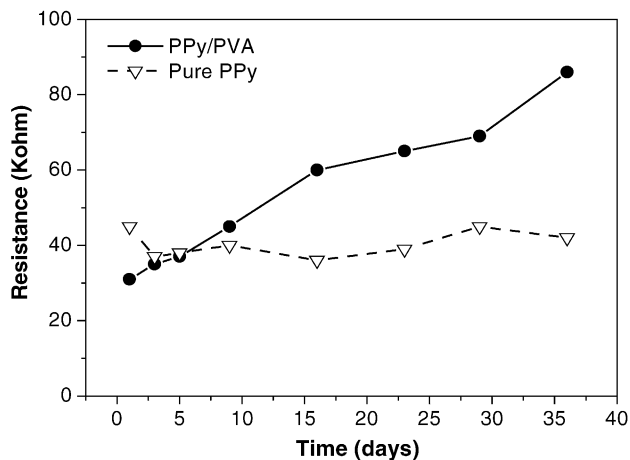


Fig. 10. Initial resistance of PPy/PVA and pure PPy sensor stored under atmosphere condition.

sion limitation, the gap between the recovery curve and the initial baseline can take place at the first test and disappear in subsequent cycles.

The two types of sensors were stored under atmosphere condition for about 1 month to investigate the long-term stability. As can be seen from Fig. 9, the stability of PPy/PVA sensor was maintained for 2 weeks and decreased gradually after that. However, the stability of pure PPy sensor was maintained over 1 month without much decay. It was thought that the hydrophilic sites on PVA were more readily bounded by moisture and other contaminants in the air, e.g. CO and CO₂, which caused an increase in sensor's resistance (Fig. 10), and worsened the activity of the composite sensor. While, the resistance of pure PPy sensor kept constant during the storage, indicating that the polymer film was not contaminated and deactivated as much as PPy/PVA composite sensor.

4. Conclusions

Conducting PPy/PVA composite and pure PPy gas sensors were prepared by in situ vapor state polymerization method. The FT-Raman spectroscopy of vapor state polymerized PPy was identical to that of chemically polymerized PPy, confirming the same chemical structure. Both types of sensors had positive sensitivity when exposed to methanol gas. The linearity between sensitivity and gas concentration was good in the range of 50–1059 ppm. The sensitivity of PPy/PVA composite sensor was higher than that of pure PPy sensor. Both the response and recovery time of PPy/PVA composite sensors were longer than those of pure PPy sensors. The thickness of the sensing film affected the sensitivity. The sensor having thinner film had higher sensitivity than that having thicker film, indicating that the resistance of polymer film involved in the sensing behavior was bulk resistance rather than surface resistance. The reproducibility of PPy/PVA composite sensor was excellent during eight on-off cycles by switching between N₂ and 3000 ppm methanol gas, indicating that our sensor could be used cyclically. The sensitivity of PPy/PVA composite sensor was only maintained for 2 weeks, while the sensitivity of pure PPy sensor was maintained over 1 month.

Acknowledgements

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