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OXIDANT EFFECTS ON POLYPYRROLE AND POLYANILINE SENSOR FOR SEVERAL VOLATILE ORGANIC GASES

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ABSTRACT

The properties of polypyrrole and polyaniline sensor made from chemical polymerization were investigated. It was found that the oxidant (ammonium persulfate) affected solubility, conductivity and the sensing characteristics of polypyrrole and polyaniline. Atomic force microscopy (AFM) was used to investigate the morphology of the sensing films. A sensor array with 6 sensors was developed to recognize various kinds and quantities of volatile organic compounds (VOCs), such as benzene, toluene and chloroform. Principal Components Analysis (PCA) was used to analyze the VOC sensing characteristics.

Key Words: Polypyrrole; Polyaniline; VOCs; APS (ammonium persulfate acid)

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INTRODUCTION

There is increasing interest in fabricating sensors to detect, identify and quantify volatile chemicals. Artificial nose prototypes have been already constructed and used in the field, ranging from quality control of foods and beverages to monitoring of specific industrial environment gases for safety.[1] Accordingly, in order to monitor dangerous and toxic VOCs, high performance sensors and systems are required that can identify and measure various kinds and quantities of VOCs. Several researchers have previously reported on the use of gas sensors in an array, such as metal oxides, electrochemical sensors, conducting polymers, field effect transistor devices, surface acoustic wave devices, and hybrid sensor array.[2–4]

Conducting polymer sensor arrays are being increasingly reported for use in odor detection and identification. Several advantages exist over other technologies such as few poisoning effects, rapid reversibility, room temperature operation (little power consumption and no breakdown of volatiles at the sensor surface at moderate temperature), rapid response absorption/desorption and long sensor lifetime.[4] However, the understanding of chemical interactions with conducting polymers is still poor.

In this work, we investigate the sensing characteristics of polypyrrole and polyaniline with different oxidant amounts and suggest why these sensors show different sensitivities on VOCs. The sensor array, which was made by chemical polymerization, generated specific response patterns when it was exposed to VOCs gases. These patterns were processed by pattern recognition techniques and used to identify the chemical species. The characteristics of the multi-dimensional sensor signals obtained from each sensor were analyzed using the principal component analysis (PCA) technique.

EXPERIMENTAL

Sensor Fabrication

Polypyrrole and polyaniline were prepared by chemical polymerization based on Lee's method.[5] Ammonium persulfate (APS, Kanto Chemical Co.) as an oxidant and dodecylbenzene sulfonic acid (DBSA, Kanto Chemical Co. Inc.) as a dopant were used as received. 0.15 mol of DBSA and 0.3 mol of pyrrole or aniline were dissolved in 500 mL of distilled water by stirring vigorously. APS in 100 mL of distilled water was slowly added to the above solution at 0°C. The reaction was carried out for 12 h and terminated by pouring methanol into the solution. The resultant polypyrrole or polyaniline powder was washed sequentially with distilled water, methanol and acetone, followed by filtering and drying in a vacuum oven at 25°C for 12 h.

Table 1. Specifications of the Sensors Utilized in the Array

Sample No.	Polymer Type	Additive Amount (APS)	Conductivity (S/cm)	Solubility in Chloroform
1	Polypyrrole	0.059 mol	2.2×10^{-4}	99%
2	Polypyrrole	0.082 mol	6.7×10^{-4}	99%
3	Polypyrrole	0.090 mol	1.6×10^{-2}	97%
4	Polyaniline	0.12 mol	2.8×10^{-4}	98%
5	Polyaniline	0.15 mol	7.4×10^{-4}	98%
6	Polyaniline	0.18 mol	2.0×10^{-3}	92%
7	Polypyrrole	0.10 mol	–	28%
8	Polypyrrole	0.15 mol	–	13%
9	Polypyrrole	0.045 mol	7.7×10^{-5}	99%
10	Polyaniline	0.21 mol	–	75%
11	Polyaniline	0.26 mol	–	28%
12	Polyaniline	0.086 mol	8.3×10^{-5}	98%

Several polymer sensor materials based on polypyrrole and polyaniline were made by changing the amounts of additive oxidant (APS) shown in Table 1. A sensor array was consisted of sample no. 1–6 sensor.
Each sensor was made as follows:

The powder obtained (0.1 g) was completely dissolved by ultrasonification in 5 mL of chloroform with an additional 0.2 g of DBSA. The solution was transferred onto an alumina substrate with a comb-type electrode of a 0.5 mm gap between each other. The solvent was removed in a N_2 purged oven at 0°C, resulting in a film with a thickness of about 1 μm. The film cast from the chloroform solution was washed with acetone to leach out the extra DBSA.

Measurements

Flow injection systems were used to obtain the VOC signals as shown in Fig. 1. The vaporizing temperature was set at 6°C using a water bath. Two mass flow controllers (MFCs) were employed along with N_2 as the carrier gas. The sensor array characteristics were then tested in a testing chamber after flow injection of the VOC vapor. The sensor signals were monitored by a personal computer with a DAQ board. The multi-sensors signal characteristics were also analyzed using PCA technique.[6] The sensitivity was defined as $((R_{N_2} - R_{gas})/R_{N_2}) \times 100$ (%), where R_{N_2}, R_{gas} are the electrical resistances in nitrogen gas and VOC, respectively.

Electrical conductivity of the film was measured by the four-probe method. Surface morphology of the films were studied by an atomic force microscope (Nanoscope IIIa).

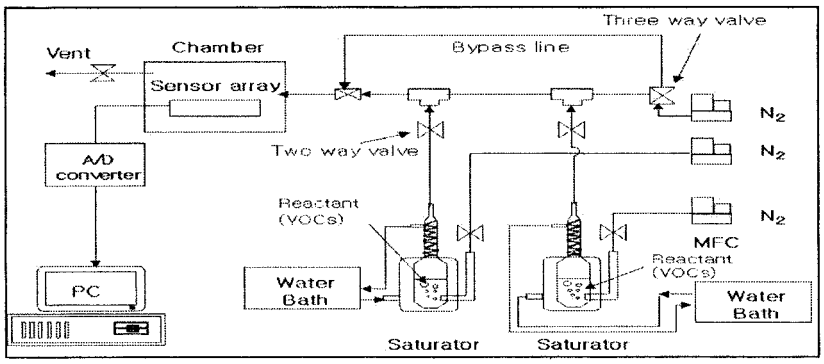


Figure 1. Schematic diagram for measuring the properties of a sensor array.

RESULTS AND DISCUSSION

In this work, the amounts of monomer (pyrrole, aniline) and DBAS were fixed. The conducting polymer characteristics dependent on oxidant (APS) concentration were investigated. The conducting polymer solubility in an organic solvent (chloroform) was affected by the amounts of APS. Each type of polymer (polypyrrole and polyaniline) had a critical point of solubility. In polypyrrole, 0.090 mol of APS was the critical point of solubility and in polyaniline, 0.18 mol of APS was the critical point. Over the critical point, the conducting polymer solubility decreased as shown in Table 1. The conductivity of conducting polymer also changed relative to the APS amount. A large APS amount generates higher film conductivity. With small APS amounts, the film conductivities of films were too low to use as a gas sensor. To fabricate the sensor array, sample no. 1, 2, 3, 4, 5 and 6 were selected. Sample no. 7, 8, 9, 10, 11 and 12 removed from the sensor array because of their poor solubility and low conductivity. The response time of a sensor to gas is directly related to gas detection and classification. The time response curve of the sensor array to 3000 ppm toluene at 20°C, as shown in Fig. 2, shows that the gas reaction was completed after 30 secs, whereas desorption of the gas was finished after about 1 min.

Each sensor shows the different sensitivities for VOC gases as shown in Fig. 3. The polypyrrole sensors show positive sensitivities in contrast to the negative sensitivities of the polyaniline sensors. In other words, polypyrrole conductivity increases but polyaniline conductivity decreases when VOC gases are exposed.

The propagation of polymer chains proceeds by a redox process between the growing chain (as an oxidant) and aniline, pyrrole (as a reducer) with the addition of a monomer to the chain end.[7] The oxidant (ammonium persulfate)/pyrrole, aniline ratio (APS/An, Py) affects the degree of

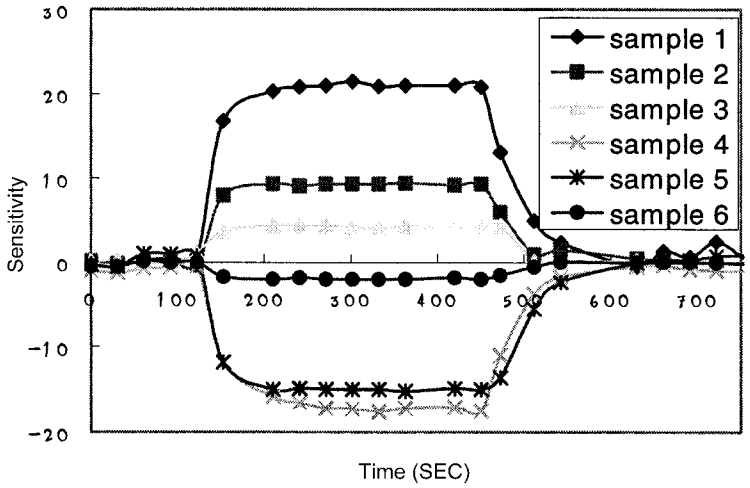


Figure 2. Time response of sensors with 3000-ppm toluene.

oxidation and polymer molecular weight (polymerization degree).[8] The sensitivity of each sensor depended on the oxidant amount, as shown in Fig. 3. This can be explained by the fact that the polymerization degree affects the conducting polymer film sensitivity.[9] This result corresponds with the previous results that the sensitivity of an oligomer is higher than a polymer.[10] The sensitivity of a chemically polymerized sensor increases for benzene, chloroform and toluene in the order of polarity of the absorbed molecules, as shown in Fig. 4. This can be explained by the fact that more polar molecules have a greater effect on the polymer chain.

The carrier (polaron and bipolaron) concentration of polymer films and its effects on VOC sensing were investigated with UV-Vis spectroscopy as shown in Fig. 5. Around the 400-nm and 800-nm wavelengths, an absorption area was generated by the carrier effects in polypyrrole. In polyaniline, it appears around the 700-nm wavelength. The carrier concentration of each polymer film decreased in the order of sample no. 3, 2, 1 and 6, 5, 4 in the polypyrrole and polyaniline, compared with the integral value, respectively as shown in Fig. 5. The carrier concentration of polymer films affects the conductivity of each film. Thus, the conductivities of sample no. 3 and 6 , which have more carrier than sample no. 1 and 3, are higher than sample no. 1 and 3, respectively.

The films cast from the soluble polypyrrole and polyaniline exhibited different morphological characteristics, observed by atomic force microscopy (AFM). The film cast from the soluble polypyrrole exhibits a smoother surface than the polyaniline. The oxidant concentration affected the surface morphology. As mentioned above, the oxidant concentration affects the

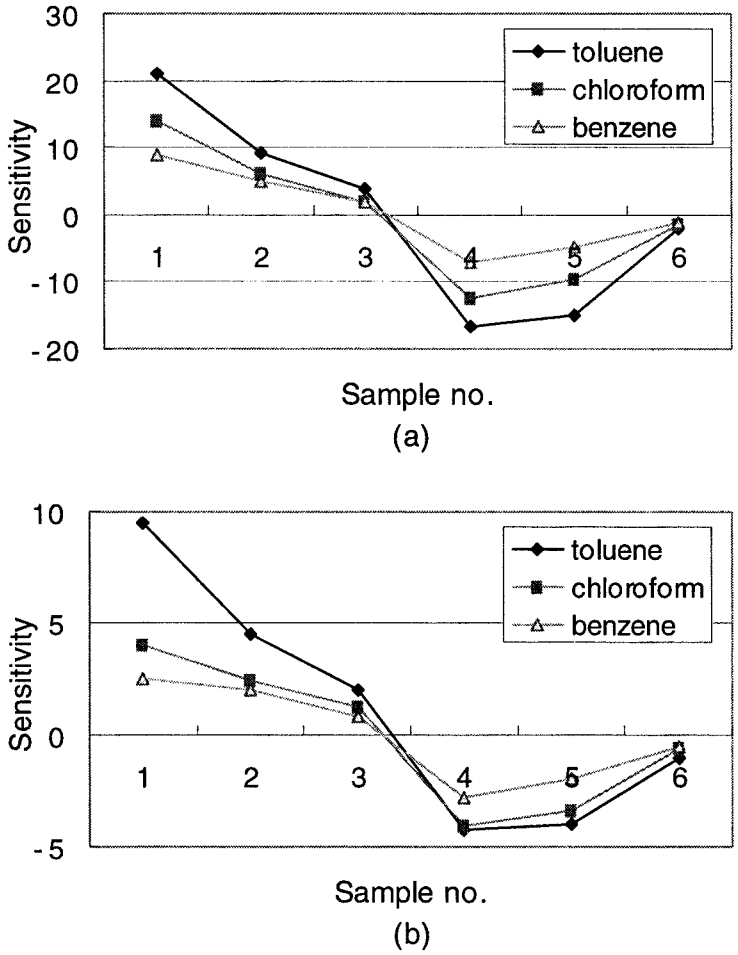


Figure 3. Sensitivity of 6 sensor array to VOC gases; (a) 3000-ppm, (b) 1000-ppm.

polymer molecular weight. The polymers (sample no. 3 and 6) with higher molecular weight exhibited coarser surface than the lower ones (sample no. 1 and 4), as shown in Figs. 6 and 7.

Classification of the gas compound species and quantity can be achieved through PCA, which enables mapping multi-dimensional data onto 2- or 3-D axes with a minimum loss of information, as shown in Fig. 8. This demonstrates the ability of PCA to classify benzene, toluene, chloroform gases with concentration of 1000 ppm and 3000 ppm.

Most of the conducting polymers can be considered a p-type semiconductor, therefore the main carriers are the polaron and the bipolaron as the positive carrier which move along the polymer chain.[4] In contrast, polyaniline is a n-type conducting polymer. Gas absorption on the surface is considered to affect the conductivity of the polymer sensors. First, the carrier

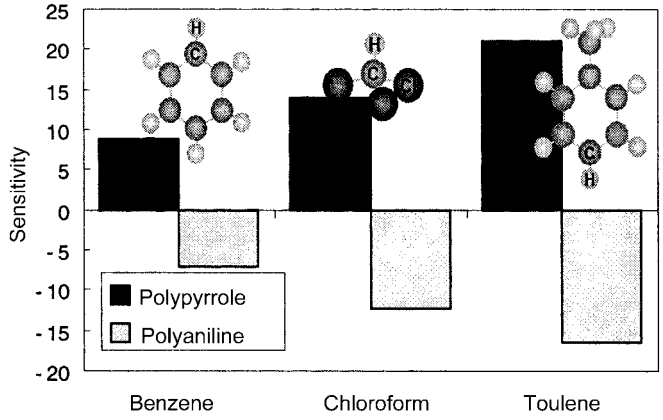
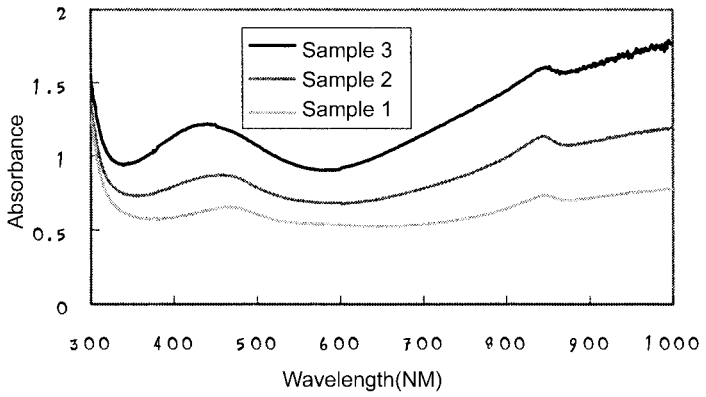


Figure 4. Sensitivity of each sensor type (polypyrrole, polyaniline) for 3000-ppm benzene, chloroform, and toluene.



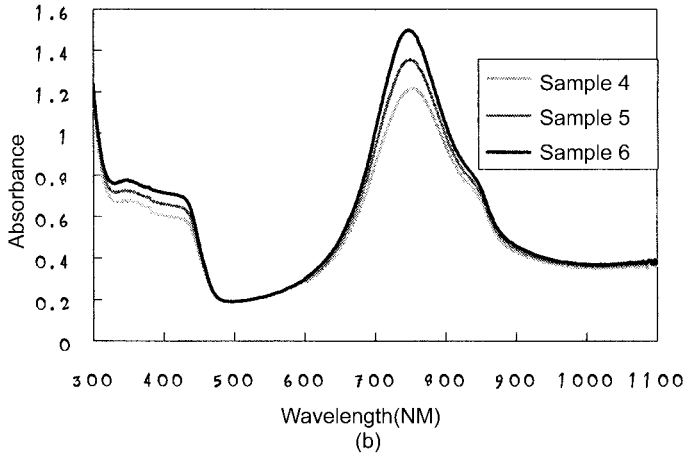


Figure 5. UV-Vis spectra of soluble (a) polypyrrole, (b) polyaniline.

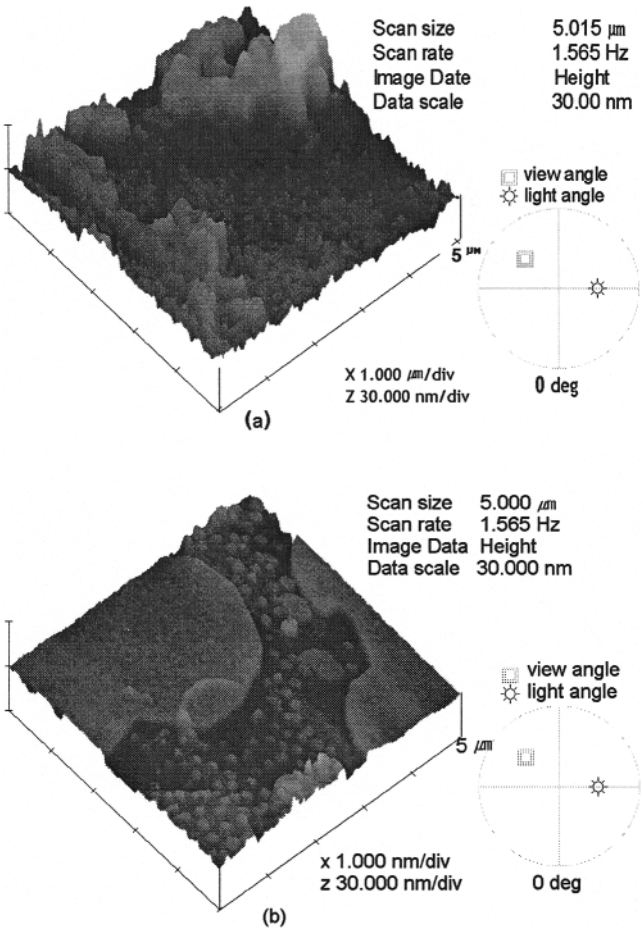


Figure 6. AFM picture of the cast film surface of chemically polymerized soluble polypyrrole; (a) Sample no. 3, (b) Sample no. 1.

movement is interrupted by the absorption of gas. Second, the absorbed gases change the surface property of polymers by rendering defects (such as polaron and bipolaron which affect the conductivity and sensitivity). In the case of polypyrrole, the first is the dominant effect, but in the case of polyaniline, the second is dominant. Thus, polypyrrole exhibits positive sensitivity, whereas polyaniline exhibits the negative sensitivity.

The oxidant affects the molecular weight. The gases can be absorbed and desorbed at the end of the polymer chain, this is the main effect of the sensitivity change. If the molecular weight increases, the site of gas absorption/desorption will decrease in the same area of film, thus the sensitivity of polymer can be affected by the oxidant.

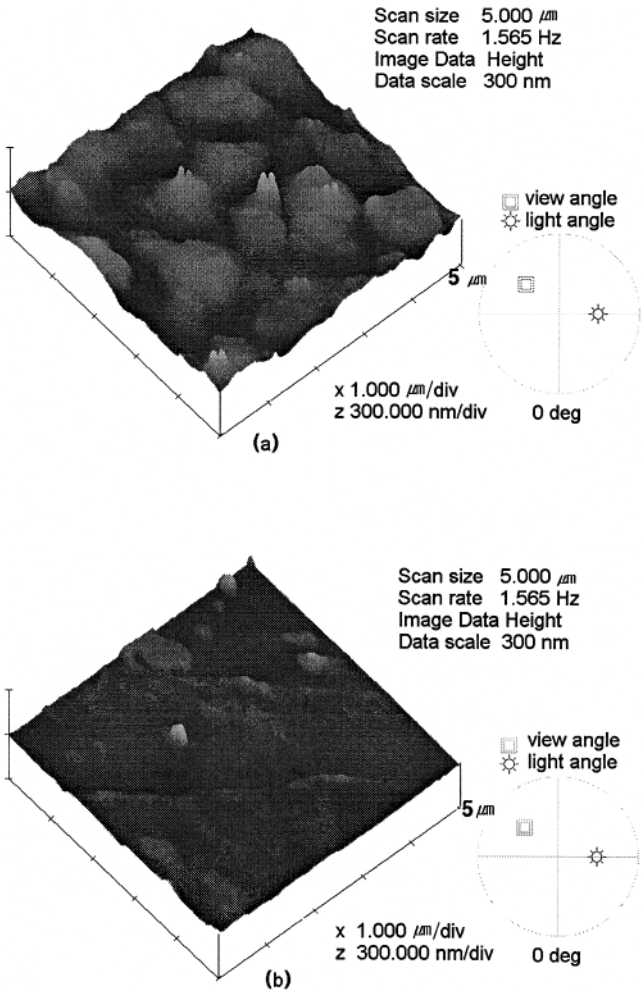


Figure 7. AFM picture of the cast film surface of chemically polymerized soluble polyaniline; (a) Sample no. 6, (b) Sample no. 4.

CONCLUSION

A VOC-monitoring system, including a sensor array which was made by polypyrrole and polyaniline, was fabricated and the sensing characteristics depending on the oxidant amount were investigated. Polypyrrole has positive sensitivity, whereas polyaniline has negative sensitivity. The absolute sensitivity was in proportion to the amounts of oxidant (APS). The polymerization degree of polypyrrole and polyaniline affected the morphology of the films. The sensitivities depended on the polar degree of gases molecular. The sensing characteristics of VOC gases could be classified by PCA. Polypyrrole is polycationic compound and polyaniline is polyanionic polymer. The

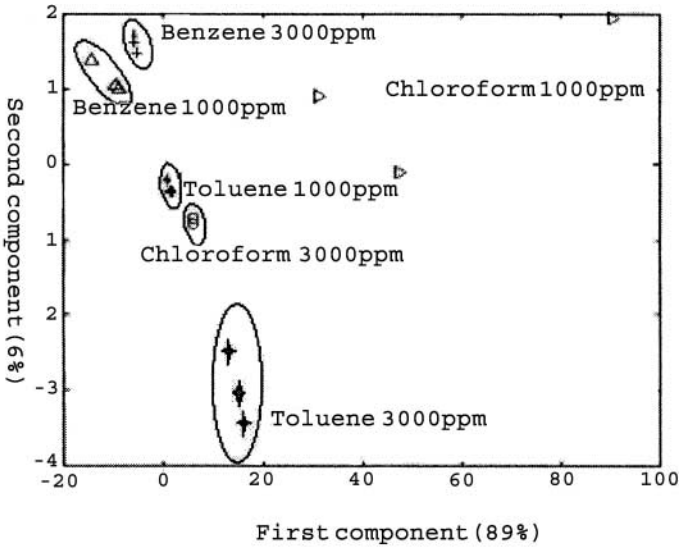


Figure 8. PCA results of sensing data from sensor array.

difference in conducting polymers exhibited different response to specific gases. When gases were absorbed to two different types of conducting polymers, opposite sensitivity was observed. By utilizing the above findings, we are able to develop more accurate and sensitive sensors.

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