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Development of PPy Films Doped with Thiol-SAM-Cu Particles for NH_3 Gas Sensing

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We have developed a high-sensitivity polypyrrole (PPy) film with a porous structure using a simple and easy method of doping thiol self-assembled monolayer (SAM)-Cu particles into a PPy film. The thiol-Cu-SAM particles were doped by the adsorption of thioxylenol or decanethiol into the porous PPy film surface, resulting in an improvement in sensitivity of the film to NH_3. Owing to the addition of thiol-Cu-SAM particles formed using various 4-*tert*-butylcalix-6-arene thiol derivatives, the sensitivity correspondingly decreased. In particular, for the case of poly(propylene oxide)-calix-6-arenethiol, a marked decrease in sensitivity was observed. Using this composite nanomaterial, we found that the detection limit for NH_3 increased to concentration levels of several ppm. We present a novel preparation method for these sensor films aimed at controlling their porosity and sensitivity.

1. Introduction

Conducting polymers, such as polypyrrole (PPy) and polythiophene (PTh), are of interest because of their high response to various gases at room temperature, and their easy modification for gas sensing. However, the sensitivity and selectivity of these gas sensors is lower than those of conventional inorganic-semiconductor-based gas sensors. To improve the sensitivity and selectivity of conducting polymer-based gas sensors, we have

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developed gas sensor devices that combine a metal-doped inorganic semiconductor (Pt- and Pd-doped SnO_2) and a conducting polymer (PTh and derivatives) with a micro-heater array structure fabricated using a silicon surface micromachining technique.(1,2) To meet the needs of chemical processes and biological systems, however, it is necessary to improve the performance of each gas sensing material. In particular, for NH_3 detection, Penza *et al.*(3,4) have reported an improvement in the detection limit up to a concentration of 100 ppm using PPy films with a well-ordered porous structure fabricated using the Langmuir-Blodgett (LB) method. This result shows that the surface properties of a sensor film are closely connected to its gas sensitivity.(1,3–6)

Therefore, we sought to develop a high-sensitivity PPy film with a porous structure using a simple and easy fabrication method, such as doping thiol self-assembled monolayer (SAM)-Cu particles into a PPy film.(7–10) In general, thiol-SAM-Cu particles offer tremendous potential for controlling surface chemical structure and associated interfacial interactions. They are chemically robust, well-ordered materials that are easily prepared. In addition, they present stable, well-defined surfaces. As a result, we succeeded in fabricating novel gas sensing materials with a nanoporous structure by doping thiol-SAM-Cu particles into PPy films. Using this composite nanomaterial, we found that the detection limit for NH_3 jumped to a concentration of several ppm. In this paper, we describe a novel preparation method for these sensor films, focusing on the control of porosity and sensitivity.

2. Materials and Method

2.1 *Chemicals*

The pyrrole was purchased from Wako Pure Chemical Industries (Osaka, Japan). The 4-*tert*-butylcalix-6-arene was purchased from Aldrich Chemical Co. Ltd, USA. The poly (propylene oxide) (Mw. *ca.* 2,000), amino poly (*N*-isopropylacrylamide) (Mw. *ca.* 1,000), decanethiol, thioxyrenol, mercaptoethanol, and tetra-n-butyl ammonium perchlorate (Bu_4NClO_4) were purchased from Tokyo Kasei Kogyo Co. Ltd, Japan. The Cu particles (ϕ = 50 nm) were purchased from Nilaco Co. Ltd. (Tokyo, Japan). Solvents and other chemicals were of analytical grade and were used without any other purification.

2.2 *Synthesis of series of thiol derivatives of calix-6-arene*

2.2.1 *Synthesis of 4-tert-butylcalix-6-arenethiol (calixthiol)*

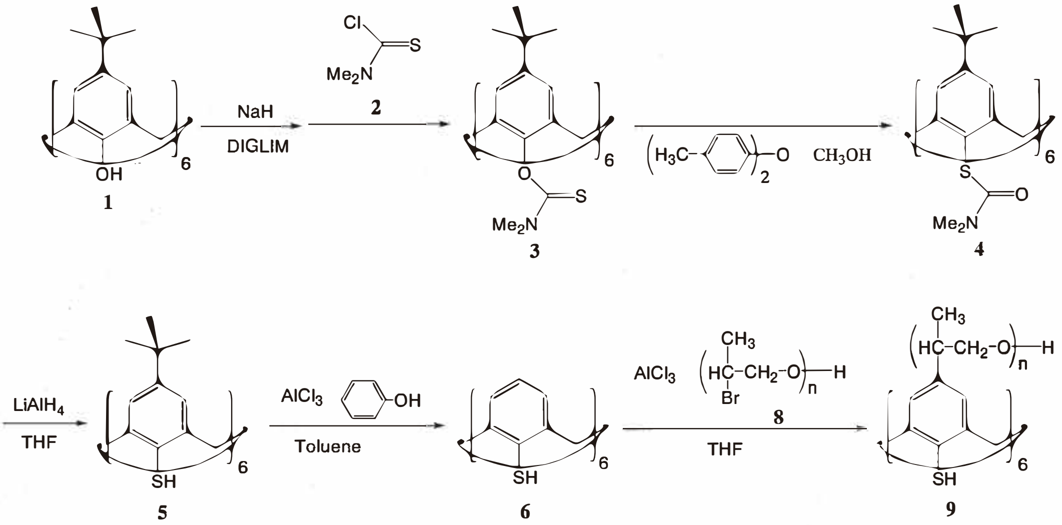
The thiolation of 4-*tert*-butylcalix-6-arene was performed according to procedures described in the literature.(11,12) After 1.375 g of NaH was dissolved in 125 ml of di(ethyleneglycol) dimethyl ether (diglyme), 5.0 g of 4-*tert*-butylcalix-6-arene, compound **1**, was added, and the solution was refluxed for 90 min. Then 40 ml of N, N-dimethyl (thiocarbamoyl)chloride, compound **2**, was added to this solution and the mixture was refluxed for 18 h. Compound **3** was obtained by flash chromatography carried out eleven times (solvent = dichloromethane/petroleum ether, yield = 3.63 g). Compound **3** was dissolved in a mixture of 200 ml of p-tolyl ether and 100 ml of methanol, and this solution was refluxed for 72 h at 130–135°C. Compound **4** was obtained by flash chromatography carried out eleven times (solvent = dichloromethane/petroleum ether, yield = 3.43 g). A mass of 1.73 g of $LiAlH_4$ was dissolved in 170 ml of tetrahydrofuran (THF), compound **4** was then added, and the solution was refluxed for 8 h. After refluxing, excess ethyl acetate and sulfuric acid were added to the solution to remove any unreacted $LiAlH_4$. Compound **5** was obtained by extraction with dichloromethane and flash chromatography (yield = 2.53 g, IR = 2250 cm^{-1} (S-H bond)).

2.2.2 *Synthesis of 4-poly (propylene oxide)-calix-6-arenethiol (PPO-calixthiol)*

A mass of 2.53 g of $AlCl_3$ was dissolved in 25 ml of toluene, and 2.53 g of compound **5** and 2.0 g of phenol were added. This solution was then refluxed for 8 h. After refluxing, 50 ml of water and 50 ml of methanol were added to this solution to decompose any unreacted $AlCl_3$. Then, 4-debutylcalix-6-arenethiol, compound **6**, was obtained by extraction with diethyl ether, and separation using column chromatography (1:9 ethyl acetate/ petroleum ether, yield = 1.14 g (68.8 %)).

A mass of 8.0 g of poly (propylene oxide) (Mw = *ca* 2,000) **7** and 9 ml of phosphorous tribromide (PBr_3) were dissolved in 80 ml of N, N-dimethylformamide (DMF). This solution was then refluxed for 12 h. A volume of 20 ml of water and 20 ml of methanol were added to this solution to decompose any unreacted PBr_3. Then, compound **8** was obtained by extraction with diethylether followed by column chromatography (eluent = 1:9 ethyl acetate/petroleum ether). Yield = 6.22 g (77.5%), IR = 620 cm^{-1} (C-Br bond).

A mass of 1.33 g of dried $AlCl_3$, 0.3 g of compound **6**, and 6.0 g of compound **8** were dissolved in 50 ml of THF, and this solution was refluxed for 10 h. The unreacted $AlCl_3$ was decomposed by adding 25 ml of water and 25 ml of methanol. PPO-calix-6-arenethiol, compound **9**, was obtained by extraction using column chromatography, as described above, (yield = 3.35 g (58.7%), IR = the disappearance of C-Br bonding ($\nu_{C\text{-}Br} = 620\ cm^{-1}$)).

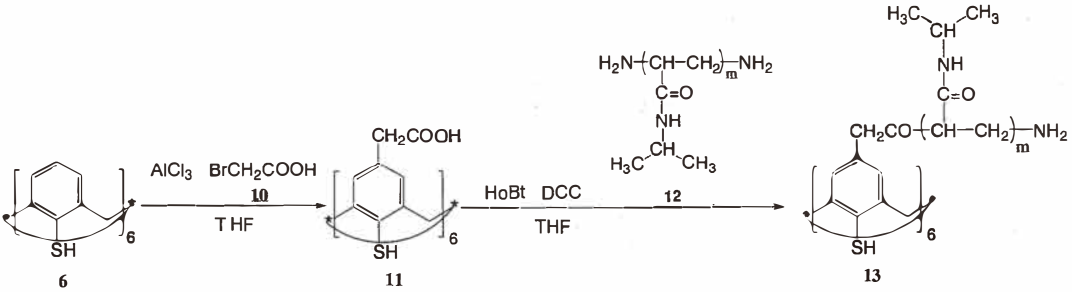


Scheme 1. Synthesis of compounds **6** and **9**.

2.2.3 *Synthesis of 4-N-isopropylacrylamide-calix-6-arenethiol (NIPAM-calixthiol)*

A mass of 6.0 g of glycolic acid ($HOCH_2COOH$) was dissolved in 90 ml of methanol; 2.8 ml of sulfunic acid was then added to this solution which was subsequently refluxed for 1 h. The reaction of glycolic acid was confirmed using thin-layer chromatography (1:1 ethyl acetate/hexane). A mass of 6.98 g of glycolic acid methyl ester ($HOCH_2COOCH_3$) was obtained by extraction using a water/diethylether mixture(50:35 ml), followed by the removal of the solvent. Then, 6.98 g of glycolic acid methyl ester was mixed with 4.5 ml of PBr_3 in 40 ml of DMF, and this solution was refluxed for 12 h. Any unreacted PBr_3 was removed by adding a water/methanol mixture (10:10 ml). The solvent was removed after 12 h, and 1-bromomethylacetate ($BrCH_2COOCH_3$) was obtained using column chromatography. A volume of 40 ml of water and 2 ml of sulfuric acid were added to this solution, and this was refluxed for 12 h. The mixture was then freeze-dried with 3.0 g of NaOH. A mixture of 50 ml of water and 35 ml of diethylether were added to this solution. After extraction and removal of the solvent, light brown crystals of 1-bromoacetic acid ($BrCH_2COOH$), compound **10**, were obtained (yield = 1.12 g (10.4%), IR = 636 cm^{-1} (C-Br), 1760 cm^{-1} (CO), and 3500 cm^{-1} (OH)).

A mass of 0.1 g of $AlCl_3$ and 0.625 g of compound **10** were dissolved in 16 ml of THF. Then, 0.35 g of compound **6** was added to this solution, which was then refluxed for 12 h. After refluxing, the mixture was extracted with a water/diethylether mixture, and compound **11** was obtained (yield = 0.48 g(88.9%)). A mass of 0.34 g of compound **11**, 0.34 g of amino-poly (*N*-isopropylacrylamide) (Mw = *ca* 1,000), compound **12**, 0.07 g of 1-hydroxy-1H-benzotriazole (HOBt), and 0.09 g of dicyclohexylcarbodiimide (DCC) were dissolved in 40 ml of THF. After 12 h of incubation at room temperature, water and diethylether were added to this solution. After extraction, removal of the diethylether, column chromatography, and freeze-drying, compound **13** was obtained (yield = 0.25 g, (37%), IR = 3300 cm^{-1} (O=C-NH-R), 2800 cm^{-1} (–CH_2–C=O), 1500 cm^{-1} (–Ar)).



Scheme 2. Synthesis of compound **13**.

2.3 *Preparation of thiol-SAM-Cu particles*

The thiol-SAM-Cu particles were prepared as follows.(11–14) One hundred milligrams of Cu particles ($\phi = 50$ nm) and 1 mM of compound **6** were placed in 2 ml of ethanol. Other thiols, compounds **9** and **13**, decanethiol compound **14**, mercaptoethanol compound **15**, and thioxyrenol compound **16**, were also used (see Fig. 1).

2.4 *Evaluation of thiol-SAM-Cu particles*

The formation of thiol-SAM-Cu particles was confirmed using a fluorescence method employing 1-anilinonaphtalene-8-sulfonic acid (ANS). A volume of 0.2 ml of an ethanol solution containing thiol-SAM-Cu particles was added to 100 mM of a Tris-HCl buffer solution (pH = 7.5) to form a final concentration of copper particles of 10 mg/ml. The ANS-ethanol solution was then added to a solution of ethanol containing 20 μM of thiol-SAM-Cu particles. The ANS fluorescence was measured using fluorescence spectroscopy, employing a Jasco FP 6500 spectrometer (Jasco Co. Ltd, Japan) at an excitation wavelength of $\lambda = 400$ nm and an emission wavelength of $\lambda = 470$ nm.

2.5 *Preparation of PPy films doped with thiol-SAM-Cu particles*

Electrochemical polymerization was performed using an HA-151 potentiostat/galvanostat (Hokuto Denko, Japan) with Ag/AgCl reference electrodes (Model 91-03, Orion, Japan) and a platinum counter electrode. The working electrode was a patterned indium tin oxide (ITO) electrode, in which an isolation gap of 10 μm was formed using photolithography, as shown in Fig. 2.(2)

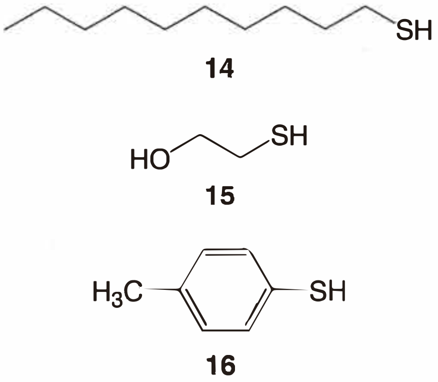


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Fig. 1. Chemical structures of decanethiol, compound **14**; mercaptoethanol, compound **15**; and thioxyrenol, compound **16**.

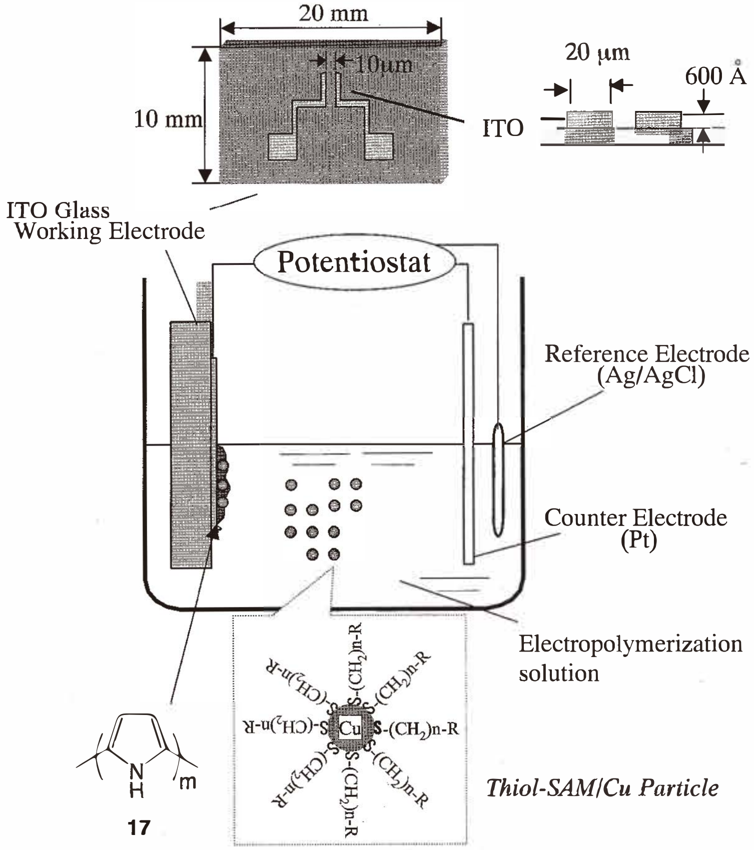


Fig. 2. Preparation of PPy film doped with thiol-SAM/Cu particles.

The PPy, compound **17**, (see Fig. 2) was obtained from a solution of 0.05 M of pyrrole in acetonitrile containing 0.15 M Bu_4NClO_4 as an electrolyte, operating at a potential of 1.6 V at a temperature of T = 25°C for 5 min.(12,13) The Cu particles and/or a variety of thiol-SAM-Cu particles were added as doping agents. A PPy film was only obtained at a potential of 1.4 V.

2.6 *Observation of surface properties of hybrid films*

Micrographs of the surfaces of several hybrid films were obtained using a scanning electron microscope (SEM) (Hitachi, Model S-2250, Japan). Compositional analysis of the electrically conductive polymer films was performed using electron-dispersed spectrometry (EDS) (Nihon Phillips EDAX, Japan).

2.7 *Gas response of hybrid films*

The gas response of various hybrid films was evaluated from the changes in resistance as reported in the literature.(1,2) In brief, the change in the resistance of the films was measured in air containing NH_3 gas at 25°C ($[NH_3] = 0.2$–500 ppm). After exposing the film to this gas for 10 min, the gas chamber was flushed with clean air at RH = 65% for 20 min.

3. Results and Discussion

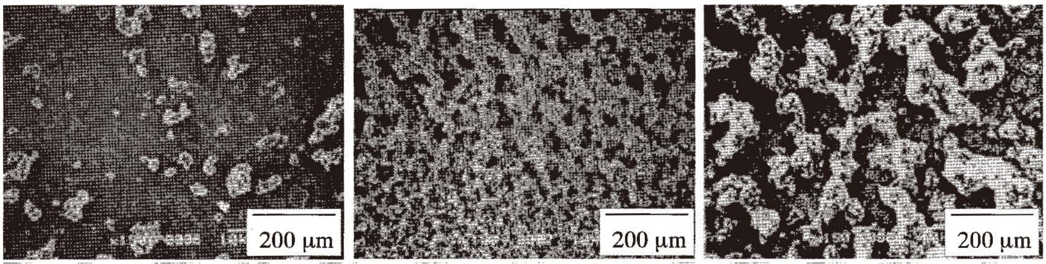
3.1 *Formation of thiol-SAM-Cu particles*

To evaluate the formation of thiol-SAM-Cu particles, we measured their hydrophobicity with ANS. The ANS fluorescence intensity provides an index of the hydrophobicity of materials, because a hydrophobic ANS molecule is preferably partitioned into a hydrophobic layer.(14) The index of hydrophobicity (RI) is defined as $RI = I/I_{\mathrm{Cu}}$, where I_{Cu} is the fluorescence intensity from a bare Cu particle, and I is the fluorescence intensity from each thiol-SAM-Cu particle. For the thiol-SAM-Cu particles, the relative RI value ($RI \sim 3$) was > 1.0, which strongly suggests that the surface of each Cu particle was made hydrophobic by the thiol-SAM moiety because the bonding of the SH group to Cu resulted in exposure of its hydrophobic part to the bulk solution. To clarify the cause of the hydrophobic modification of the Cu particles in detail, we studied two thiol derivatives: PPO-calixthiol and NIPAM-calixthiol, as PPO and NIPAM are known thermosensitive polymers. The temperature dependence of both thiol-SAM-Cu mixtures was measured, and the resulting RI values reached a maximum ($RI \sim 15$) at temperatures around $T = 30$°C for NIPAM-calixthiol/Cu. In the case of PPO-calixthiol/Cu, the RI value reached $RI \sim 10$ at around $T = 47$°C. Each characteristic temperature corresponded to a change in the conformation of the polymer. This suggests that the structural properties of the polymers were retained after hydrophobic modification of the Cu particles. On the basis of these results, we suggested that the thiol derivatives **9** and **13** bonded to the Cu via the SH group, and not the hydrophobic component, such as PPO (see compound **9**) and NIPAM (see compound **13**). As a result, we concluded that the thiol derivatives used in our experiments were deposited on the surface of the Cu particles through an interaction between the SH groups and the Cu surface.

3.2 *Observation of hybrid film surfaces using SEM*

The electrochemical polymerization of PPy was carried out on ITO glass electrodes.(2) The polymer film had to grow through the gap to form a resistor element between the separated electrodes.

Figures 3(a)–3(c) show SEM images of samples P1, P5, and P7. In Fig. 3(a), the surface of sample P1 appears to be very rough, less porous than the surfaces of the other samples. In Figs. 3(b) and 3(c), the surfaces of samples P5 and P7 appear to be more homogeneous and porous than that of sample P1. In particular, as shown in Fig. 3(b), the surface of sample P5 was the most homogeneous and porous of all the films. The modification with thiol-SAM clearly influences the microstructure of PPy films.



(a) P1 (b) P5 (c) P7

Fig. 3. SEM images of typical PPy films.

However, significant data concerning the surface area and porosity of the films were not obtained, because *in situ* measurements of the films were very difficult.

3.3 *Compositional analysis of hybrid films using EDS*

To investigate whether Cu and/or thiol-SAM-Cu particles were immobilized on the PPy films, composition analysis using EDS was performed, and the results are summarized in Table 1. Immobilization of the thiol-SAM-Cu particle was evaluated by considering the fraction of Cu and/or sulfur (S, for the thiols) as a marker. From the data presented in Table 1, significant fractions of Cu and S were confirmed, suggesting that thiol-SAM-Cu particle was immobilized in the PPy films. In the results for samples P3–P8, the Cu content, in general, was less than that of bare Cu (sample P2).

Calixthiol was used as a model to clarify how the steric effect derived from the molecular shape of the thiol derivatives influenced the polymerization process. Calixthiol is a thiol derivative of calix-6-arene with a benzene ring. A small increase in thiol content relative to the Cu content of samples P6, P7, and P8 was detected, whereas an S content from the thiol compounds of 14.78% was immobilized with a Cu content of 0.47% in sample P5. The small concentration of calixthiol in both samples P7 and P8 is validated by considering two points: (1) PPOcalixthiol(P7) and NIPAMcalixthiol(P8) has a higher molecule weight than other compounds; and (2) calixthiol is hydrophobic and has a large steric hindrance. However, the detailed structures of the hybrid films are unknown.

3.4 *Gas response of hybrid film*

The electrical resistances of eight PPy films are summarized in Table 2. Sample P1 had the highest resistivity, and sample P2 the lowest because of the presence of conducting Cu particles. The resistivities of the other hybrid films were between those of samples P1 and P2. Samples P3, P4, and P5 showed approximately the same resistivity, as did samples P6, P7, and P8. In addition, the resistivities of samples P3, P4 and P5 that contained small molecule thiol-SAM-Cu particles were lower than those of samples P6, P7 and P8 that contained polymeric thiol-SAM-Cu particles.

Table 1
EDS results of Cu and S content (%) of PPy films doped with thiol-SAM /Cu particles.

PPy	P1	P2	P3	P4	P5	P6	P7	P8
Cu	—	11.46	3.30	1.75	0.47	3.68	2.22	0.52
S	—	—	0.87	0.81	14.78	0.67	0.06	0.012

Key: "—" = Cu and/or thiol-SAM /Cu particles were not included in the original PPy film.

Table 2
Resistivity of PPy films.

PPy	Additive	Resistance [kΩ]
P1	None	3.20
P2	Cu particle	0.21
P3	Mercaptoethanol, **15**/Cu	0.56
P4	Decanethiol, **14**/Cu	0.43
P5	Thioxyrenol, **16**/Cu	0.51
P6	Calixthiol, **6**/Cu	0.72
P7	PPOcalixthiol, **9**/Cu	0.83
P8	NIPAMcalixthiol, **13**/Cu	0.81

To study the gas response of the hybrid films, the change in electrical resistance was measured both before and after injection of NH_3 gas into the experimental chamber. The sensitivity, S, is defined as $S = \Delta R/R_{base}$, where R_{base} is the resistance of the sample in air, and ΔR denotes the change in resistance from the base resistance after injection of NH_3 gas into the chamber.

The PPy films were so stable that their electrical resistance was constant during the first five minutes, and when NH_3 gas ($[NH_3] = 100$ ppm) was introduced into the experimental chamber, a marked increase in resistance was observed.

For sample P4 (decanethiol) and sample P5 (thioxyrenol), the maximum values of $\Delta R/R_{base}$ were higher than that of sample P1. Taking the microstructures of these films into consideration, we found that the more porous the hybrid film, the higher the sensitivity observed.

In the case of sample P2 (Cu alone), the sensitivity decreased. In samples P6, P7 and P8, on the other hand, the values of S were lower than those of the PPy films, indicating that there was no improvement in sensitivity to NH_3 gas. This suggests that the hydrophobicity and the steric hindrance inhibit the interaction between NH_3 and the PPy films, which, together with Cu, are not sensitive to NH_3 gas.

Figure 4 shows the dependence of $\Delta R_{max}/R_{base}$ on the NH_3 gas concentration for various films. The value of ΔR_{max} is the maximum resistivity observed (the saturated value) after injection of NH_3 gas. From Fig. 4, sample P1 exhibited a change in resistance for

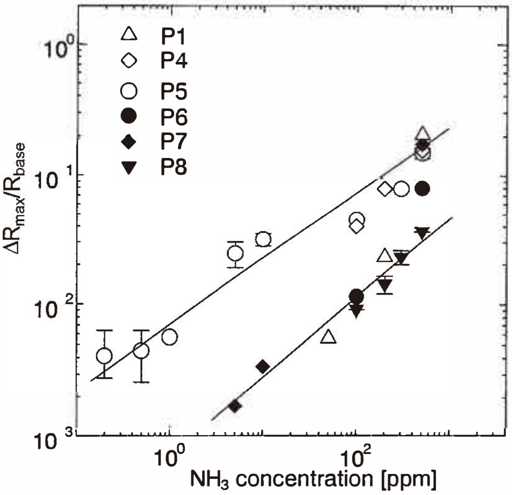


Fig. 4. The dependence of normalized resistance for various sensor films on NH_3.

concentrations of several tens of ppm. In samples P6–P8, the detection limit was improved up to concentrations of several ppm, but the sensitivity was lowered. In samples P4 and P5, the detection limit was improved further, especially in sample P5, and reproducible measurements were taken with an accuracy in the sub ppm range. We suggest that for sample P5, the high sensitivity observed was due to the π conjugation in the benzene ring of thioxyrenol and the molecular size of thioxyrenol. The π conjugation affected the conductivity of PPy, and the molecular size provided a passage for the penetration of NH_3 molecules.

In a previous paper, we reported that the electrostatic interaction between the ammonium ion (NH_4^+) and an electrolyte (ClO_4^-) may contribute to a change in the resistance of PTh films after the injection of ammonia gas.(2) In the case of PPy films, the mechanism for the change in resistance in the presence of ammonia gas is considered to be similar to that of PTh films. The doping of thiol-SAM-Cu particles changed the sensitivity of the films to NH_3 gas by making the PPy films porous, and the resulting area-to-volume ratio of the sensor film increased. In addition, the electronic environment of the prepared film was changed by the electron-donating properties of the thiol-SAM-Cu particles. The coverage of Cu particles from the thiol molecules influences the electronic state of the entire PPy film. The hydrophobic part of the thiol molecules plays an important role in sensing NH_3. In addition, we found that PPy films containing only Cu particles had low resistivity, and their ability to sense NH_3 was the lowest of all our samples. Doping with thiol-SAM-Cu particle changes the sensitivityof the films to NH_3 gas. Further studies on the precise NH_3 sensing mechanism of other thiol-SAM-Cu particles are in progress.

4. Conclusions

We have developed a highly sensitive PPy film with a porous structure by the simple and easy method of doping thiol-SAM-Cu particles into PPy films. Modification of the the film with thiol-SAM-Cu particles influences the behavior of the PPy film as a sensor, but the microstructures of the films have a uniform and very fine structure. For example, upon doping with Cu-SAM, formed by the adsorption of thioxylenol or decanethiol into the PPy films, the film surface was porous, resulting in an improvement in the sensitivity of the films to NH_3 gas, whereas the addition of Cu-SAM formed from various thiol derivatives of 4-*tert*-butylcalix-6-arene made the sensitivity correspondingly decrease. Using this nanocomposite material, we have succeeded in increasing the detection limit for NH_3 to concentrations of several ppm, and we have established a novel systematic preparation method for sensor films, focusing on microstructural control.

Acknowledgments

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References

1 Y. Sakurai, H.-S. Jung, T. Shimanouchi, T. Inoguchi, S. Morita, R. Kuboi and K. Natsukawa: Sensors and Actuators B, **83** (2002) 270.
2 H.-S. Jung, T. Shimanouchi, S. Morita, R. Kuboi: Electroanalysis **15** (2003) 1453.
3 M. Penza, E. Milella, M. B. Alba, A. Quirini and L. Vasanelli: Sensors and Actuators B **40** (1997) 205.
4 E. Milella and M. Penza: Thin Solid Films **327** (1998) 694.
5 J. Maso, N. Barniol, F. Perez-Murano and X. Aymeric: Thin Solid Films **261** (1995) 299.
6 A. Guadarrama, M. Rodriguez-Mendez, C. Sanz, J. Rios and J. Saja: Anal. Chem. Acta. **432** (2001) 283.
7 M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidesey: J. Am. Chem. Soc., **109** (1987) 3559.
8 J-H. Li, J.-H. Yang, W.-Q. Yan, S.-J. Chen and C. Dong: Chin. J. Chem. **15** (1997) 131.
9 A. Ulman: Chem. Rev. **96** (1996) 1533.
10 P. E. Laibins and G. M. Whitesides: J. Am. Chem. Soc. **114** (1992) 1990.
11 C. G. Gibbs and C. D. Gutsche: J. Am. Chem. Soc. **115** (1993) 5338.
12 C. G. Gibbs, P. K. Sujeeth, J. S. Rogers, C. G. Stanley, M. Krawiec, W. H. Watson and C. D. Gutsche: J. Org. Chem. **60** (1995) 8394.
13 G. Tourillon and F. Garnier: J. Electroanal. Chem. **135** (1982) 173.
14 M. Yoshimoto, R. Kuboi, Q. Yang and J. Miyake: J. Chromatogr. B **712** (1998) 59.