

Optical Gas Sensors using Environmental Indicator-Polymer Composites

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To detect ppm or ppb concentrations of ammonia and hydrogen chloride, and relative humidity, several optochemical gas sensors operating at room temperature have been developed. The last ten years results in our group are summarized.

Key Words: Chemical sensor, Humidity, Ammonia, Hydrogen chloride, Environmental indicators

Introduction

Recently to measure ppm or ppb concentrations of gases, various optochemical sensors operating at room temperature have been presented. Chemical sensors fabricated on optical fiber offer several advantages, i.e. the sensors are electrically safe and the signals do not fluctuate due to electrical disturbances. In general, most optical chemical sensors are based on the principles of either absorption or fluorescence of well known indicators dispersed in polymer matrices. The choice of the indicator (probe) and of the polymer as matrix is a key question in the development of this type of sensor.

1. Composite Film with Hydrolysed Nafion and Dye with a Terminal N-phenyl Group¹⁻⁴⁾

We have proposed that a hydrolysed Nafion thin film with dyes is applicable to an optical humidity sensor. By using dyes with terminal N-phenyl groups (auxochrome) and diphenyl carbonium ions or cyanine groups (chromophore), humidity can be detected as a change in the optical intensity in visible light. By using composite films of hydrolysed Nafion and dyes having cyanine or triphenyl structures and with a terminal N-phenyl group, an optical humidity sensor has been fabricated. In the reflection mode, the optical intensity of the absorption peaks which depend on the used dyes decrease with relative humidity. The raising and recovery times are less than 1 min. In dry air, alkyl amine group reacted with SO_3H of hydrolysed Nafion and formed a proton additive. Sorption of water molecules induces the deprotonation of the quaternized ammonium group.

It is well known that crystal violet and malachite green undergo solvatochromism in which the color is very sensitive to the acidity of protons. For the composite film, the dye was entrapped as a result of the formation of a new ionic salt and the solubility of the dye in water was extremely depressed as mentioned. Crystal violet and malachite green are intensely colored violet and green in neutral water,

respectively, and in the entrapped dyes on hydrolysed Nafion; both dyes are slightly yellowish in dry air. It is expected that the acid

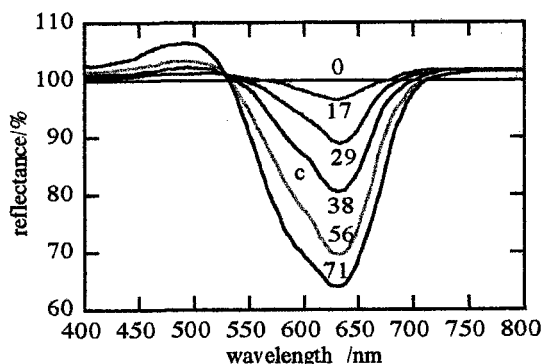


Fig.1-A Spectral changes of Nafion-Crystal Violet composite with humidity. Humidity is indicated in the figure.

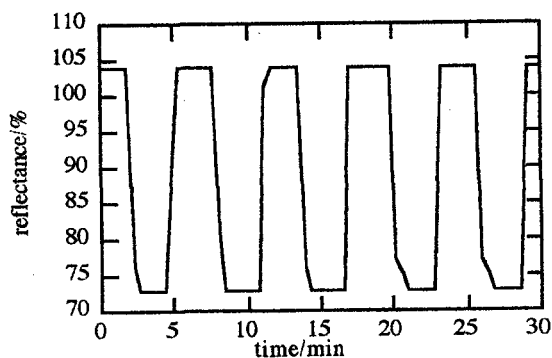


Fig.1-B. Response to the changes of humidity from 0%RH to 50 %RH and repeated for Nafion-crystal violet composite.

strength of the solid acid is weakened by the sorption of water molecules and this change induced a color change in the dyes caused by the change in the molecular structure. In a dry atmosphere, the protons of sulphonic acid form a salt with two of the terminal N-phenyl groups of crystal violet (yellowish), and the sorbed water induce a change of the quaternized ammonium to alkyl amine, i.e. deprotonation. In this case, the degree of the deprotonation is accelerated with increasing water content. The spectra in the reflection mode of the composites were examined as a function of the relative humidity. A reflection minimum was observed at 630 nm with a shoulder at 585 nm for crystal violet, at 535 nm with a shoulder at 590 nm for ethyl violet and at 610 nm for malachite green. For crystal violet entrapped on hydrolysed Nafion, the color was changed by the sorption of water molecules from violet to green with increased humidity, and good reversibility for the humidity changes was observed. The reflectance at 630 nm decreased with increasing humidity and the reverse tendency was confirmed at 470 nm, although the former signal was more sensitive than that of the latter. In addition, an isosbestic point was observed at 525 nm for crystal violet, at 540 nm for ethyl violet and at 540 nm for malachite green. These observed results convinced us that the reaction caused by the sorption of water is in equilibration for the composite with triphenyl dyes. The differences (hysteresis) in the intensity observed in the humidification and desiccation processes are very small. Spectral changes and response behavior are shown in Fig. 1-A, B for crystal violet composites.

2. Sulphonaphthaleine Dyes^{5,6)}

2.1. Effects of Humidity on Optical Characteristics of the Composites

For PVP composite thin film, the reflectance at around 470 nm due to the acidic form decreased with an increase in humidity, while that in a longer wavelength range was almost remained almost constant except for the BPB composite thin film. For the BPB composite, the humidification induced the increase in the reflectance of the band at $\lambda_{\max} \sim 640$ nm. The decrement of the reflectance at around 470 nm is in the order CR > TB > BTB > BCP > BCG ~ BPB (bromophenol blue(BPB), bromocresol green(BCG), bromocresol purple(BCP), bromothymol blue(BTB), cresol red(CR) and thymol blue(TB)). The reflectance at around 470 nm decreased with an increase in the humidity and good reversibility was confirmed. The reflectance at around 470 nm is sensitive to humidity changes and the sensitivity is in the order of CR > TB > BTB > BCP > BCG ~ BPB for the PVP composite. By assuming that the molar absorption coefficient, ϵ , of the dissociated form is the same as that of the acidic form and the increment of the concentration of the dissociated form by the humidification is related to the difference between $pK(H_2O)$ and $pK(EtOH)$, the sensitivity to the humidity may be interpreted, i.e. the sensitivity is proportional to $\epsilon[pK(H_2O)/pK(EtOH)]$. The logarithm of $\epsilon[pK(H_2O)/pK(EtOH)]$ is then estimated to be 12.4(BPB), 12.5(BCG), 12.7(BCP), 12.8(BTB), 13.1(TB) and 13.1(CR). A fair correlation between the humidity sensitivity and the value of $\epsilon[pK(H_2O)/pK(EtOH)]$ was confirmed.

2.2. Spectral Changes with Ammonia Sorption

The spectra of BCP-PVP composite are examined (Fig.2). On exposure to ammonia gas containing air, the reflectance at 600 nm decreased and the decrement was enhanced by the humidification. The isosbestic points were observed at 500 nm. Under dry conditions, the order of the sensitivity to ammonia was BPB > BCG > BCP > BTB > CR ~ TB. While the BCB and BCG composites are preferable in the respect to sensitivity, no good reversibility in response behavior was confirmed. While for BPB and BCG composites, the optical intensity in air did not recover after exposure to ammonia, a good recovery and response behavior were confirmed for the BCP and BTB composites.

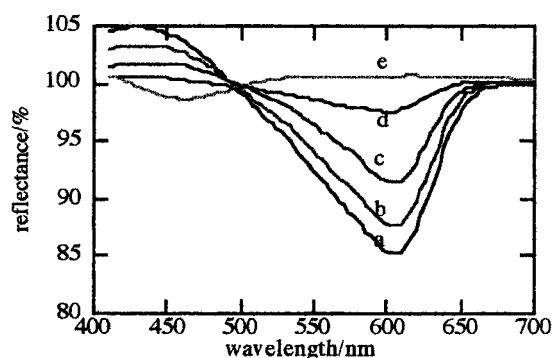


Fig. 2. Spectral changes of BCP-PVP composite.

- a) in 2500ppmNH₃/50%RH,
- b) in 1000ppmNH₃/50%RH,
- c) in 250ppmNH₃/50%RH,
- d) in 2500ppmNH₃/dry air,
- e) in 70%RH.

If the sensitivity to ammonia is only dependent on the ϵ value of the ammonia additive, it is expectable to BPB > BCP > CR > BTB > TB > BCG. The sensitivity to ammonia is in the order of BCP > BPB ~ BCG > BTB > CR > TB at 50 %RH and of BPB ~ BCG > BCP > BTB > CR at 0%RH. The sensitivity is controlled by the ϵ and the acidity.

2.3. Effects of Polymer Matrix on the Sensitivities

The sensitivities to humidity and/or ammonia vapor are influenced by the polarity, hydrogen bond acidity or hydrophilicity of the polymer as a matrix. For the composite thin films with buromoxylenol blue(BXB), the spectrum observed in 250 ppm NH₃ containing 50 %RH air is also examined (Fig.3). The sensitivity to ammonia was in the order of PEO > CAB > PVP > PMMA and the value of $\lambda_{\max}$ is also dependent on the polymer species. It seems that the equilibrium of the acid-base reaction and the dissociation degree of the dye are influenced by the polymer species. For the samples, the absorption band at $\lambda_{\max} = 420$ nm was observed with a small band at around 580 nm. While the $\lambda_{\max}$ values observed for the composite films were slightly shorter than that for the solution. The band with $\lambda_{\max} = 420$ nm was assigned to the acidic form and that at $\lambda_{\max} = 580$ nm to the basic form. From the results, the absorbance ratio, Abs(580nm)/Abs(420nm), was estimated to be 0.49, 0.15, 0.10 and 0.06 for PEO, CAB, PMMA and PVP, respectively. These values suggests

that the equilibrium constant of the acid-base reaction, $K = [\text{basic form}]/[\text{acidic form}]$, for the dye entrapped in polymer is in the order of $\text{PEO} > \text{CAB} > \text{PMMA} > \text{PVP}$. For a constant concentration of sorbed ammonia, it is expected that the sensitivity to ammonia is in the order $\text{PEO} > \text{CAB} > \text{PMMA} > \text{PVP}$. A reliable coincidence between the expected order and the observed result in dry air was confirmed. At 50 %RH, the sensitivity was in the order $\text{PEO} > \text{CAB} > \text{PVP} > \text{PMMA}$. The disagreement for PVP and PMMA may be explained by the differences in the ability to sorp waters. The ammonia gain may be accelerated by the humidification. Actually, the water sorption ability is in the order of $\text{PVP} > \text{PEO} > \text{CAB} > \text{PMMA}$.

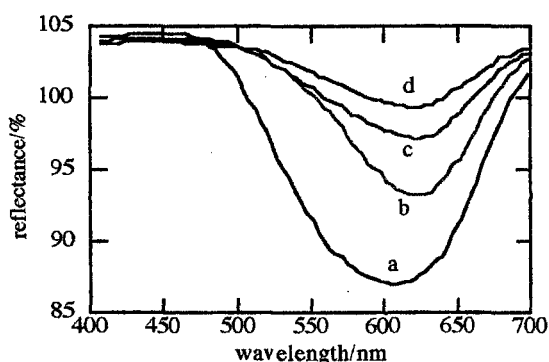


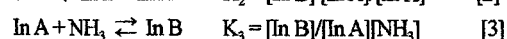
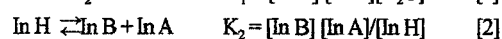
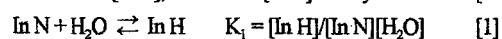
Fig.3. Spectra of BXB copposites in 50 %RH air containing 250 ppm NH_3 .
a) PEO, b) CAB, c) PVP, d) PMMA

2.4. Effects of Humidity on the Sensitivity to Ammonia

As mentioned, the humidification induced the enhancement of the reflectance at around 640 nm in the reflection mode for the BPB composite. This is caused by the decrease in the concentration of the basic form. From the pH dependence of the absorbance of the dye in solution, the sensitivity to ammonia of the PVP composite is expected to be $\text{BCP} > \text{BPB} > \text{BCG} > \text{BTB} > \text{CR} > \text{TB}$ which is in fair agreement with the order of the sensitivity to ammonia at 50 %RH. The sensitivity to ammonia is enhanced by humidification. The sorption of the water induces the enhancement of the degree of dissociation of the neutral form. The dissociated form can interact or react with ammonia and resulting in the formation of the basic form. In this model, it is considered that the neutral form only weakly interacts with ammonia molecules.

2.5. Sensing Mechanism

The absorption spectrum of the composite film is sensitive to humidity and ammonia gas. A good linear relationship between the absorbance and the logarithm of ammonia concentration was observed. The slope of this straight line (sensitivity) increased with increasing humidity. Under humid conditions, the dye exists as a mixture of acidic form $[\text{In A}]$, basic form $[\text{In B}]$ and hydrated form $[\text{In H}]$, i.e.



where $[\text{In N}]$ is the concentration of neutral form, $[\text{H}_2\text{O}]$ and $[\text{NH}_3]$ are

the concentrations of sorbed water and ammonia, respectively. When the ammonia content is proportional to the logarithm of ammonia concentration in air, $[\text{NH}_3] = K_4 \log (C_{\text{NH}_3})$, it is expected that the absorbance is proportional to the logarithm of C_{NH_3} . Furthermore, the water gain of PVP linearly increases with relative humidity, i.e. $[\text{H}_2\text{O}] = K_5 [\% \text{RH}]$. As denoted above, the dye exists in the acidic form under ammonia free conditions, i.e., $[\text{In A}] \gg [\text{In B}]$, so that equation [2] can be replaced by eq. [2']



Finally, it is expected that the absorbance is proportional to $[\text{In N}][\% \text{RH}][\log C_{\text{NH}_3}]$.

The expected relationship convinced us about dependence of the absorbance at 605 nm on the humidity and ammonia concentration. It is clarified that the spectral changes of BCP-PVP composite are based on the acid-base equilibrium.

3. Tetraphenylporphine⁷⁻¹⁷⁾

3.1. Absorption Spectrum of Ethyl Cellulose-Composite

The absorption spectra of the composites were examined. Both Soret band ($\lambda_{\text{max}} = 416 \text{ nm}$) with a shoulder at 395 nm and the Q-bands ($\lambda_{\text{max}} = 515, 549, 590 \text{ and } 646 \text{ nm}$) were observed for the TPPH_2 -composite. The absorption spectrum is influenced by the TPPH_2

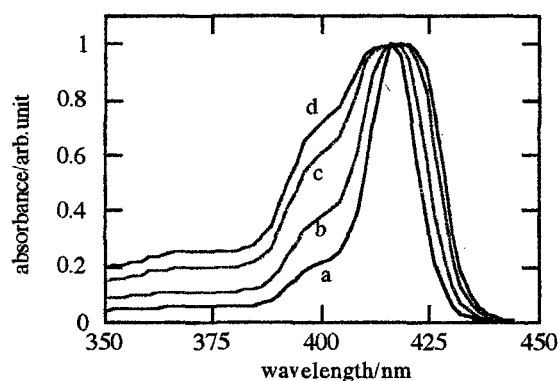


Fig.4-A. Absorption spectra of the TPPH_2 -EC composite.

a) $1 \times 10^{-5} \text{ mol/gEC}$, b) $4 \times 10^{-5} \text{ mol/gEC}$,
c) $7 \times 10^{-5} \text{ mol/gEC}$, d) $14 \times 10^{-5} \text{ mol/gEC}$.

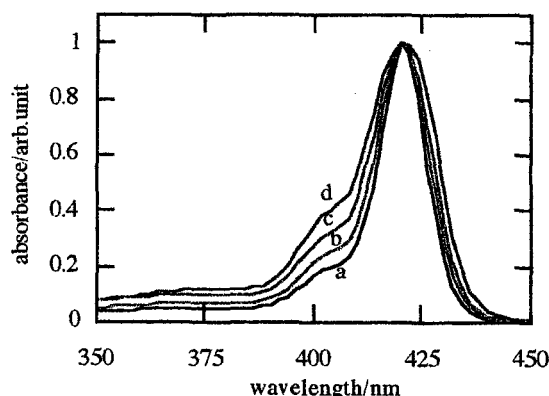


Fig.4-B. Absorption spectra of the TP(Br)PH_2 -EC composite.

a) $1 \times 10^{-5} \text{ mol/gEC}$, b) $4 \times 10^{-5} \text{ mol/gEC}$,
c) $7 \times 10^{-5} \text{ mol/gEC}$, d) $14 \times 10^{-5} \text{ mol/gEC}$.

concentration as shown in Fig. 4-A. For the film with 1×10^{-5} mol/g, the Soret band is observed at 416 nm with a shoulder at 395 nm. The half-width of the Soret band is similar to that of the DMF solution (5×10^{-6} mol/dm³) i.e. the plane-plane interactions between porphine molecules are weak. With increasing concentration, the Soret band is split and λ_{max} is observed at 414 and 419 nm with the shoulder at the shorter wavelength. The spectral changes with concentration are related to the intermolecular interactions, e.g., concentration-dependent aggregation (sandwich-type and in-plane-type interaction). For the TP(Br)PH₂ composite, the Soret band is observed at 420 nm with a shoulder in the lower wavelength region. The half-width of the Soret band is only slightly increased with concentration. Splitting of the Soret band was not observed (Fig. 4-B). It appears that the bromination of the phenyl group to depresses the intermolecular interaction/aggregation. For TP(OH)PH₂ composite, the Soret band ($\lambda_{\text{max}} = 422$ nm) with a shoulder at 405 nm and the Q-bands were observed. With increasing concentration, broadening of the band is observed with a splitting of the Soret band. This suggests the formation of the associated species (sandwich-type and in-plane-type interaction).

3.2. Spectral Changes with Acidic Vapors.

For the benzene solution (5×10^{-3} dm³) with 5×10^{-6} mol/dm³ of TPPH₂, enhancement of the absorbance at $\lambda_{\text{max}} = 656$ nm and red-shift (from 416 nm to 448 nm) of the Soret band were observed by adding conc. HCl (1×10^{-6} dm³) to the solution (λ_{max} of the Soret band: 439 nm for conc. HNO₃ (1×10^{-6} dm³) and 435 nm for conc. HF (1×10^{-6} dm³)). Adding of 7×10^{-6} dm³ of conc. HCOOH, CH₃COOH and C₂H₅COOH resulted in no significant spectral changes. Since at this stage it is very difficult to prepare/control sub-ppm levels of acidic gases such as HNO₃, HF or organic acids, conc. acids (5×10^{-6} dm³) were placed in the cell and the absorbance was measured at room temperature.

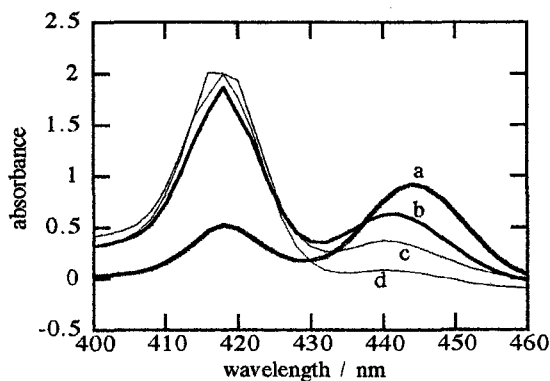


Fig. 5. Absorption spectrum of TPPH₂ composite film in acidic vapor.
a) HCl, b) HF, c) HCOOH, d) CH₃COOH.

The results are shown in Fig. 5. λ_{max} of the Soret band is influenced by the nature of the acid. It was confirmed that the system is sensitive to the vapor of HNO₃, HF and HCOOH solution but not to the vapor of CH₃COOH liquid. It is also possible to determine the nature of the acid. The highest sensitivity of the Soret band of TPPH₂ is observed for HCl. For the film containing 1×10^{-5} mol/g of TPPH₂, the reflectance at $\lambda_{\text{max}} = 450, 618$ and 664 nm decreases and the reflectance at $\lambda_{\text{max}} = 414, 548, 594$ nm increases with increasing concentration of HCl gas. These changes are completely reversible.

3.3. Effects of Substituent Group

To modify the sensitivity and λ_{max} of the band sensitive to HCl, the hydrogen in para position to the phenyl group was replaced with -OH or -Br. The spectral changes on exposure to dry HCl are shown in Figs. 6-A and -B for the composite films TP(Br)PH₂. The reflectance at $\lambda_{\text{max}} = 453, 620$ and 670 nm decreases and the reflectance at $\lambda_{\text{max}} = 510$ and 554 nm increases with increasing concentration of HCl gas. These changes are also reversible. For TP(Br)PH₂-composite, the spectral changes with HCl are essentially not influenced by the concentration of TP(Br)PH₂ even at higher HCl concentrations. As mentioned, for the TP(Br)PH₂ composite, the half-width of the Soret band is only slightly increased with increasing concentration and no splitting of the Soret band were detected. We postulate that the difference in the spectral changes between the TPPH₂ and TP(Br)PH₂-composites at the higher HCl concentration is based on the difference of the intermolecular interaction/aggregation. To detect high concentrations of dry HCl, the TP(Br)PH₂-composite is more preferable than the TPPH₂-composite. For TPPH₂-, and TP(Br)PH₂-composites, an introduction of 0.1 ppm HCl results in the decrease of only about 2 % in reflectance. To improve the sensitivity, the use of TP(OH)PH₂ is considered since HCl sorption ability may be enhanced by the existence of phenolic -OH group.

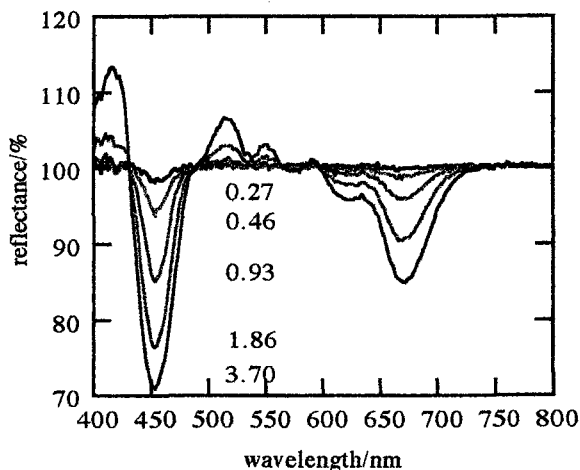


Fig. 6-A. Spectral changes of TP(Br)PH₂-composite with HCl gas.
TPBrPH₂: 4.9×10^{-5} mol/g.
HCl gas concentration in ppm is shown in the figure.

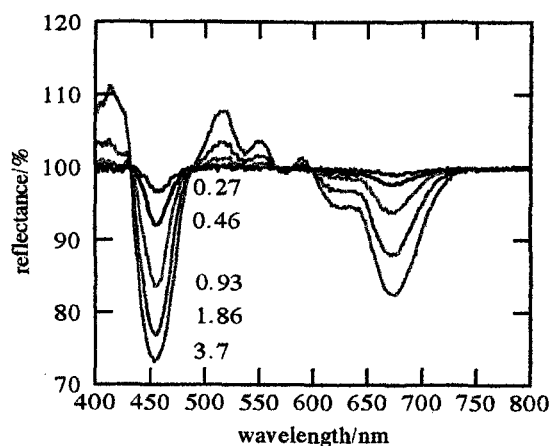


Fig.6-B. Spectral changes of TP(Br)PH₂-composite with HCl gas.

TPBrPH₂: 19×10^{-5} mol/g.

HCl gas concentration in ppm is shown in the figure.

References

- 1) Y. Sadaoka, M. Matsuguchi, and Y. Sakai, *Sensors and Actuators -A*, 25/27, (1991) 489-492
- 2) Y. Sadaoka, M. Matsuguchi, Y. Sakai, and Y. Murata, *Chemistry Letters*, 1991, 717-720
- 3) Y. Sadaoka, M. Matsuguchi, Y. Sakai, and Y. Murata, *Sensors and Actuators B*, Vol. 7, (1992) 443-446
- 4) Y. Sadaoka, M. Matsuguchi, Y. Sakai, and Y. Murata, *Journal of Materials Science*, Vol. 27, (1992) 5095-5100
- 5) Y. Sadaoka, Y. Sakai, and M. Yamada, *Journal of Materials Chemistry*, 3, (1993) 877-881
- 6) Y. Sadaoka, Y. Sakai, and X. Wang, *Journal of Materials Science*, 29, (1994) 883-886
- 7) Y. Sadaoka, N. Rodriguez, and P. Tagliatesta, *Chemistry Letters*, 1995, 509-510
- 8) Y. Sadaoka, Y. Sakai, P. Tagliatesta, and T. Boschi, *Chemistry Letters*, 1995, (1995) 907-908
- 9) P. Tagliatesta, Y. Sadaoka, and Y. Sakai, *Mol. Cryst. Liq. Cryst.*, 278, (1996) 173-180
- 10) K. Tanaka, C. Igarashi, P. Tagliatesta, T. Boschi, and Y. Sadaoka, *Journal of Materials Chemistry*, 6, (1996) 953-956
- 11) K. Nakagawa, K. Tanaka, T. Kitagawa, and Y. Sadaoka, *Journal of Materials Chemistry*, 8, (1998) 1199-1204
- 12) K. Nakagawa, T. Kitagawa, and Y. Sadaoka, *Sensors and Actuators B*, 52, (1998) 10-14
- 13) H. Supriyatno, K. Nakagawa, and Y. Sadaoka, *Electrochemistry*, 67, (1999) 431-437
- 14) K. Nakagawa, K. Kumon, C. Tsutsumi, K. Tabuchi, T. Kitagawa, and Y. Sadaoka, *Sensors and Actuators, B*, 65, (2000) 138-140
- 15) H. Supriyatono, K. Nakagawa, and Y. Sadaoka, *Sensors and Actuators, B*, 76, (2001) 36-41
- 16) K. Nakagawa, Y. Sadaoka, H. Supriyatono, A. Kubo, C. Tsutsumi, and K. Tabuchi, *Sensors and Actuators, B*, 76, (2001) 42-46
- 17) H. Supriyatono, K. Nakagawa, and Y. Sadaoka, *Sensors and Materials*, 13, (2001) 359-371

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