Optochemical HCl Gas Detection Based on Tetraphenylporphine Dispersed in Ethyl Cellulose

Yoshihiko Sadaoka, Yoshiro Sakai, Pietro Tagliatesta,† and Tristano Boschi†
Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
†Dipartimento di Scienze e Tecnologie Chimiche, Universita degli di Roma "Tor Vergata", 00173, Italy

(Received July 7, 1995)

To detect sub-ppm levels of dry HCl gas, spectral changes of tetraphenylporphine dispersed in ethylcellulose were examined in the visible region. The Soret and Q-bands of free base tetraphenylporphine are sensitive to sub-ppm levels of HCl with a good reversibility and insensitive to NH_3, Cl_2, NO_2 and NO at room temperature.

Recently various optochemical sensors that work at room temperature have been presented[1-8] for detection of industrial pollutant gases such as NO_X, Cl_2 and HCl in the order of ppm levels or below. Since phthalocyanines and structually related porphyrins have planar conjugated macrocyclic nitrogenous bases, the conductivity and/or optical behavior of thin solid films of these substances are very sensitive to the presence of the above mentioned toxic gases.[9-12] Resistive-type gas sensors based on thin films of phthalocyanine and related compounds have been studied, but practical sensors that work at room temperature with sufficient sensitivity, reversibility and fast response have not yet been reported. It seems important to prevent aggregation of these molecules in the prepared films, and when they are dispersed in polymer matrices, their agglomeration can be depressed due to weakening the plane-plane interaction between the molecules. It is known that free base porphyrin interacts with HCl and forms an acidic salt, causing changes in the optical properties. In the present work the optical properties of tetraphenylporphine dispersed in ethylcellulose were examined with respect to application for detection of sub-ppm levels of dry HCl.

Free base tetraphenylporphine ($TPPH_2$) was obtained from Aldrich Chemicals and Nakarai Co. Ltd. Ethylcellulose (EC) was obtained from Aldrich Chemicals. $TPPH_2$ and EC were dissolved in a mixture of toluene and ethanol. The solutions were coated on alumina substrates and heated at 60 °C *in vacuo* to prepare the films. The spectra of the films formed on alumina plates were measured in reflection mode. Filtered light from a D_2/I_2 lamp (400 nm ~ 800 nm) was guided into a fiber and the collected/reflected light was analyzed using a spectro multichannel photodetector (MCPD-1000, Otsuka electronics). The spectrum of the film was measured first under nitrogen and the signal intensity obtained (I_o) was used as a reference for the intensity measured in the presence of HCl. The reflectance is defined as I/I_o. All measurements were performed at 30 °C. The test gases were prepared from standard dry gases (HCl, Cl_2, NO_2, NO and NH_3) diluted with nitrogen (Sumitomo seika).

The absorption spectrum of the prepared composite of $TPPH_2$/EC under nitrogen flow was very similar to that of 5×10^{-6} mol dm^{-3} $TPPH_2$ dissolved in DMF; The half-width (14 nm) of the Soret band of the film is not so different from that of the DMF solution (12 nm) suggesting that the plane-plane interaction between porphin molecules did not seriously occur. The Q-bands with λ_{max} = 515, 549, 590 and 646 nm were observed both for

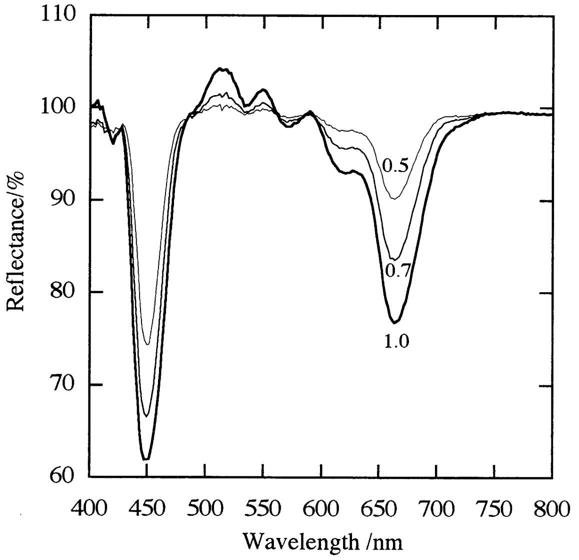

Figure 1. Spectral changes of $TPPH_2$ composite. HCl concentration in ppm is shown in the figure.

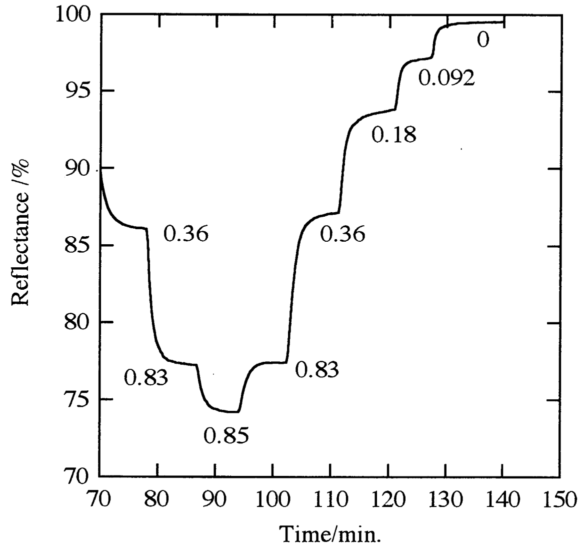

Figure 2. Reflectance changes at 450 nm with HCl of $TPPH_2$ film. HCl concentration in ppm is shown in the figure.

the EC composite and DMF solution. In 1951, Dorough et.al.[13] reported that the amphoteric nature of the porphine molecule permits the formation of acid salts with addition of protons to the center of the porphine. The spectra of these salts may be influenced by the nature of the acid (counter anion).

Spectral changes caused by HCl introduction are shown in Figure 1. The reflectance at λ = 448 nm and 665 nm decreased with an increase in the concentration of HCl gas. These changes were reversible and when HCl was cut off, the spectrum returned completely as can be recognized from reflectance change at 450 nm (Figure 2). When the film was under nitrogen flow porphin was in the free base form ($TPPH_2$). Upon exposure to HCl gas it changed into the acid salt, the degree depending on the concentration of HCl. The $\log(I_0/I)$ measured at 448 nm was proportional to HCl concentration in the range of sub-ppm levels as shown in Figure 3. For the exposure to 1 ppm of NH_3, Cl_2, NO_2 and NO/N_2, no significant changes in spectral intensity were observed between 400 nm and 800 nm.

If 10^{-3} cm^3 of conc. HCl was added to 5 cm^3 of 5×10^{-6} mol dm^{-3} $TPPH_2$ in benzene, the absorbance at λ_{max}=656 nm was enhanced and red-shifted from 416 nm to 448 nm. Similarly, the addition of 10^{-3} cm^3 of conc. HNO_3 and HF to the same $TPPH_2$ solution caused red shifts to 439 nm and 435 nm, respectively, while the addition of 7×10^{-3} cm^3 of conc. HCOOH, CH_3COOH and C_2H_5COOH resulted in no significant spectral changes. To get information on sensitivities to several acid vapors, the following experiments were carried out. The interior walls of an optical cell (1 cm^3) were coated with a $TPPH_2$/EC film and the absorbance of the film was measured. Then 5×10^{-3} cm^3 of concentrated acids were put into the cell and after equilibration of the acid vapors with the coated film the absorbance of the film was measured. The results are shown in Figure 4. As shown in the figure, λ_{max} of the Soret band is influenced by the nature of the acid. It is concluded that $TPPH_2$/EC films are also sensitive to the vapor from HNO_3, HF or HCOOH solution but not to the vapor from CH_3COOH liquid, and applicable to determine the amount of the dosed acid.

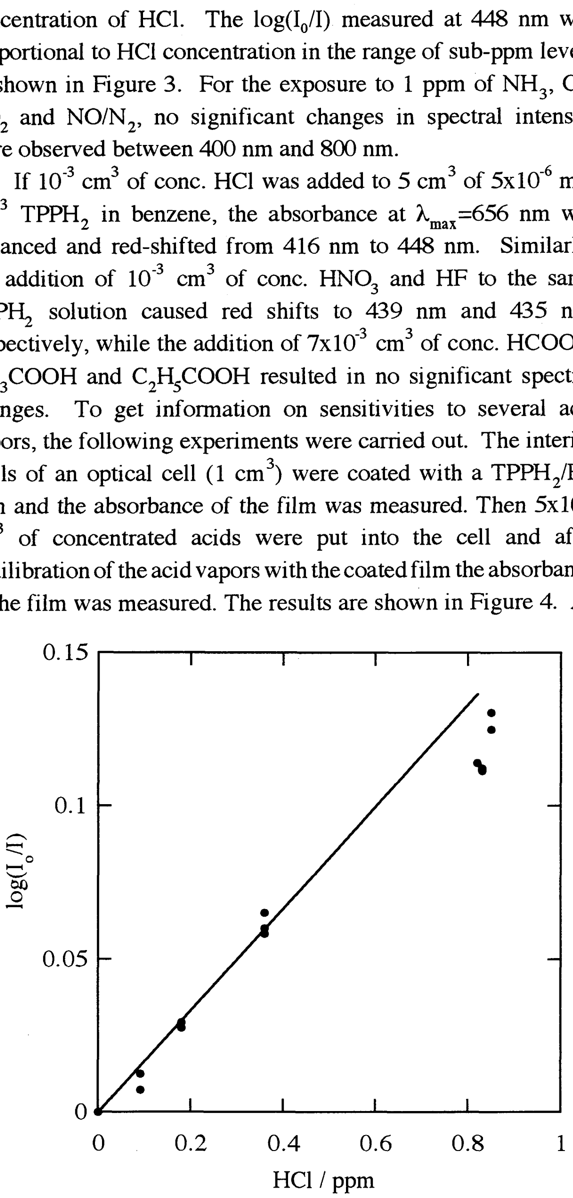

Figure 3. HCl concentration dependence of $\log(I_0/I)$ at 448 nm .

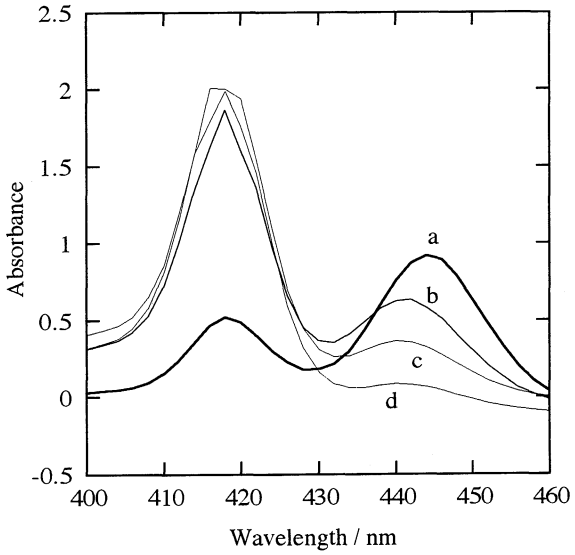

Figure 4. Absorption spectra of EC film in acidic vapor. source; a) HCl, b) HF, c) HCOOH, d) CH_3COOH.

References and Notes

1 O.S.Wolfbeis, "Fiber Optic Chemical Sensors and Biosensors I", CRC Press. Inc., Baca Raton, USA, 1991.
2 H.E.Posch and O.S.Wolfbeis, *Sens. Actuators*, **15**,77 (1988).
3 Q.Zhou, D.Kritz, L.Bonnell, and G.Siger, Jr., *Applied Optics*, **28**, 2022 (1989).
4 R.Gvishi and R.Reisfeld, *Chem. Phys. Lett.*, **156**, 181 (1989).
5 K.Wang, K.Seiler, J.P.Haug, B.Lehmann, S.West, K.Kartman, and W.Simon, *Anal. Chem.*, **63**, 970 (1991).
6 Y.Sadaoka, Y.Sakai, and Y.Murata, *Talanta*, **39**, 1675 (1992).
7 Y.Sadaoka, Y.Sakai, and M.Yamada, *J. Mater. Chem.*, **3**, 877 (1993).
8 Y.Sadaoka, Y.Sakai, and M.Yamada, *Denki Kagaku*, **62**, 1066(1994).
9 Y.Sadaoka, "Organic Semiconductor Gas Sensors," Gas Sensors, ed. by G.Sberveglieri, Kluwer Academic Pub., Dortrecht, The Netherlands (1992), P.187.
10 C.Honeybourne, R.J.Ewen, and C.A.Hill, *J. Chem. Soc., Faraday Trans. I*, **80**, 851(1984).
11 A.Moreles-Bahnik, R.Czolk, and H.J.Ache, *Sensors and Actuators, B*, **18-19**, 493(1994).
12 M.Passard, C.Maleysson, A.Pauly, S.Dogo, J.-P. Germain, and J.-P. Blanc, *Sensors and Actuators, B*, **18-19**, 489(1994).
13 G.D.Dorough, J.R. Millaer, and F.M.Huennekens, *J. Am. Chem. Soc.*, **73**,4315 (1951).