Optochemical HCl Gas Detection Based on Zinc Tetrabromotetraphenylporphyrin Dispersed in Ethyl Cellulose

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For zinc tetrabromotetraphenylporphyrin dispersed in a polymer matrix, the absorbance at 479 nm and 722 nm is sensitive to sub-ppm levels of HCl gas and also good reversibilty is observed at room temperature.

To control the emission of gaseous pollutants, analytical instruments are needed which measure the concentration of these compounds. Chemical sensors offer a promising and inexpensive way to fulfill this analytical task. Recently to measure concentrations in the order of ppm or ppb of these compounds, various optochemical sensors workable at room temperature have been presented.[1-6] Many pronounced interactions between conjugated organic compounds and gases may be classified in terms of irreversible chemical attack, reversible chemical reaction or reversible interaction. These can lead to the generation of detectable changes in physical properties of organic compounds including semiconductivity, photoconductivity, visible absorption spectra and infrared spectra. Especially for phthalocyanines and porphyrins which planar conjugated macrocyclic nitrogenous bases, conductivity and/or spectral behaviour are very sensitive to the presence of toxic gases.[7,8] The introduction of phenyl groups into *meso*-positions is effective to prevent nitration or chlorination of *meso*-positions.

Recently, it is desired to detect sub-ppm levels of HCl in exhausted gases. In the present work optical properties of immobilized zinc tetraphenylporphyrin and zinc brominated tetraphenylporphyrins were examined with respect to application for detection of sub-ppm levels of HCl.

The studied porphyrins, prepared according to known procedures were zinc tetraphenylporphyrin (TPPZn), zinc tetrabromotetraphenylporphyrin (Br_4TPPZn) and zinc octabromotetraphenylporphyrin (Br_8TPPZn).[9-11] Ethylcellulose (EC) was obtained from Aldrich Chemicals. Porphyrins and EC were dissolved in a mixture of toluene and ethanol. The solutions were used to prepare films by coating on alumina substrates or quartz plates. Afterwards the films were heated at 60 °C *in vacuo* to remove the solvent. The spectra of the element 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 (I_o) of the element in nitrogen was measured first and used as a reference for measuring the spectrum (I/I_o) of the film. The reflectance(%) was defined as 100x(I/I_o). All measurements were performed at 30 °C. The concentration of HCl or Cl_2 was controlled by mixing 10 ppm HCl or Cl_2 in nitrogen with nitrogen.

It is well known that in nonaqueous media the tetrapyrrolic macrocycle of porphine is oxidized in successive monoelectronic steps giving monocationic radicals and dications. In the case of the TPPZn, the first and second ligand oxidation potentials are 0.79 and 1.10 V *vs.* SCE for the benzonitrile solution, respectively. Oxidation/reduction behaviour is affected by the electronegativity of the porphyrin ring which is influenced by the β-substituent. In general, electron-withdrawing substituents make the oxidation of the porphyrin ligand more difficult. The Soret band with λ_{max} = 425 nm is detected for the DMF solution of TPPZn. The λ_{max} of the Soret band was red-shifted with an increase in the number of bromine substituents at the pyrrole position (λ_{max} = 436 nm for Br_4TPPZn and λ_{max} = 476 nm for Br_8TPPZn). For the composite TPPZn/EC, the absorption spectrum in nitrogen flow is very similar to that of the DMF solution (λ_{max} = 423 nm for TPPZn, λ_{max} = 436 nm for Br_4TPPZn and λ_{max} = 469 nm for Br_8TPPZn). For the composite films with EC, the half-width of the Soret band is not so different from that for the DMF solution *i.e.* the plane-plane interactions between porphin molecules are not so strong (agglomeration of the porphyrin molecules not enhanced). When HCl gas was introduced into the chamber, the spectrum of the Br_4TPPZn composite film responses to the presence of HCl. The spectral changes with HCl introduction are shown in Figure 1. The reflectance with λ_{max} = 479 and 722 nm decreases with an increase in the concentration of HCl gas. These changes are reversible and when HCl was cut off, the spectrum returned with a recovery time which is prolonged when a higher concentration of HCl gas is passed through the cell. When the sample is exposed to nitrogen flow Br_4TPPZn exists in the neutral form. By exposure to HCl gas the formation of the acid salt may proceed. In Figure 2, the reflectance changes at 479 nm and 722 nm for HCl concentration changes between 0 ppm and 5 ppm are shown. A fast response behaviour and good reversibility are observed. Furthermore, from the calibration curves it is expected that the film is applicable to detect 0.5 ppm HCl or less. For the composite with TPPZn, any apparent spectral changes in the region of 400 nm and 800 nm were not detected when HCl concentration was changed from 0 ppm to 5 ppm, and for Br_8TPPZn the reflectance at 503 nm and 739 nm only slightly decreased (about 3 %). The effect of the degree of bromination on the HCl sensitivity may be caused by the difference of distortion of the macrocycle ring.

The spectrum of the TPPZn film is influenced by Cl_2 gas and the results are shown in Figure 3. When 5 ppm Cl_2 was passed through, the reflectance at 425, 558 and 596 nm increased and that at 463 nm and 790 nm decreased. After a cut of the Cl_2 gas, the spectrum c (in Fig.3) was observed *i.e.* the reflectance at 425 nm and 800 nm recovered slightly while the reflectance at 445 nm remains. A similar behaviour is also observed for Br_4TPPZn and Br_8TPPZn where these changes are observed at longer wavelengths. The absorption spectra of TPPZn and its cation radical in CH_2Cl_2 were reported.[12] The reported spectral changes caused by the formation of the cation radical are very similar to the results observed for the TPPZn film. In this work, the formation of the cation radical of TPPZn was not examined by using other techniques such as ESR but the spectral changes by Cl_2 are interpretable in terms of the formation of the cation radical of TPPZn. The spectrum of Br_xTPPZn is very sensitive to Cl_2 but no good recovering behaviour is confirmed at room temperature.

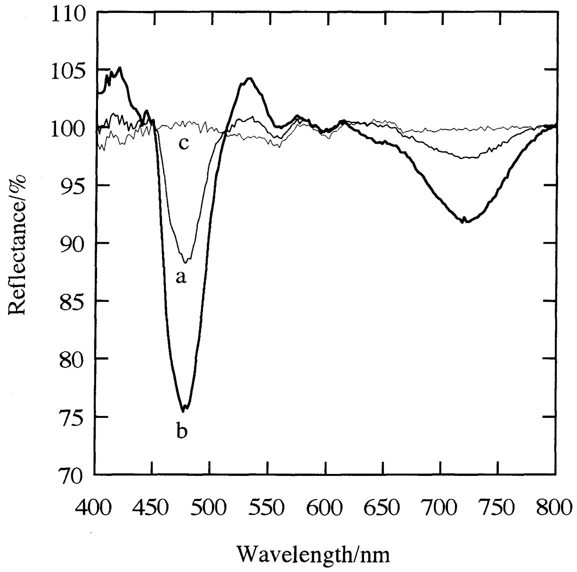

Figure1. Spectral changes with HCl of Br_4TPPZn.
a)0.5ppm, b)5ppm, c)N_2 after exposed to 5ppmHCl.

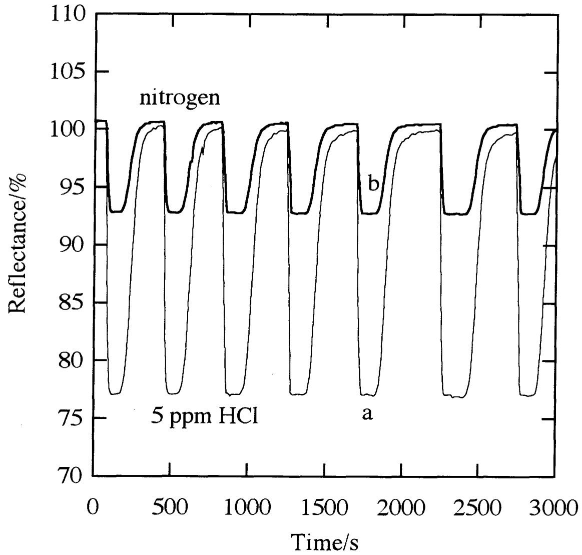

Figure2. Response behaviour of Br_4TPPZn film.
a) 479 nm, b) 722 nm.

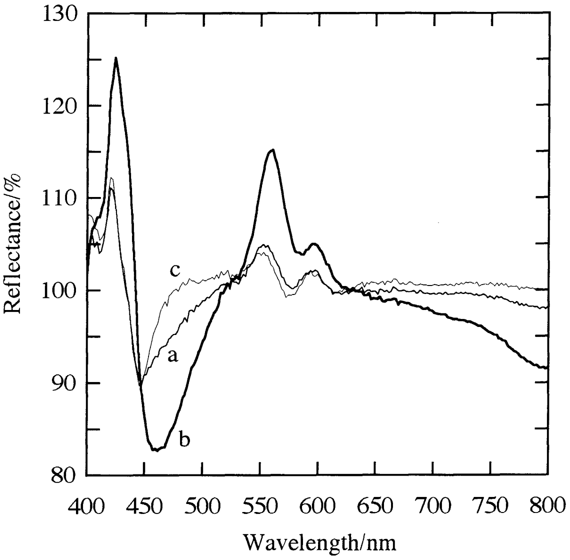

Figure3. Spectral changes with Cl_2 of TPPZn film.
a) 0.5ppm b) 5ppm, c) N_2 after exposed to 5 ppm Cl_2.

References and Notes

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