CHEMISTRY LETTERS, pp. 521-524, 1988.

Optical Detection of Nitrogen Monoxide by Metal Porphine Dispersed in Amorphous Silica Film

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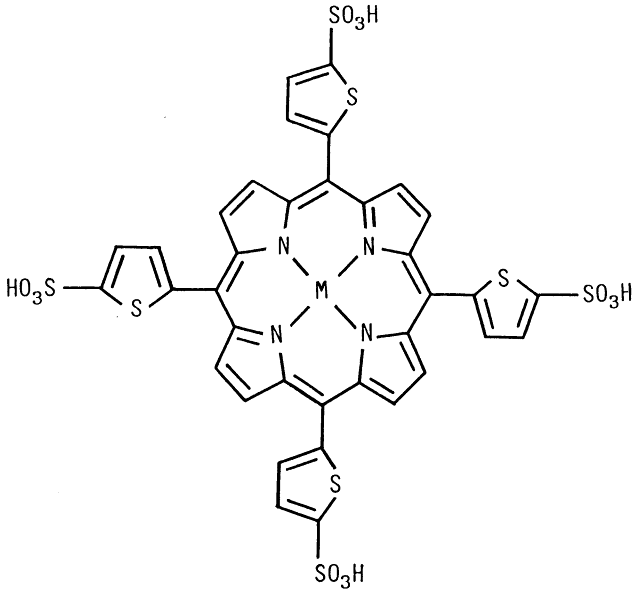
New optical detection of nitrogen monoxide was developed using cobalt α, β, γ, δ-tetrakis (5-sulfothienyl) porphine which was doped in a silica thin film by a sol-gel method. The absorption band at λ =420 nm was weakened significantly by a contact with gaseous NO at 200 °C but was not sensitive to O_2 and CO. The band change was completely reversible and depended on the pressure of NO in the pressure range of 1.3 to 3.2×10^3 Pa.

Of many types of gas sensors, those which utilize electrical or electrochemical information of materials are most often adopted for solid state sensors.[1,2] But a new method of gas detection which utilize optical properties is drawing attention quite recently. In optical solid state gas detectors, optical information of gas sensitive materials, such as absorbance or luminescence intensity is guided to detectors by an optical fiber. For such purposes, a matrix which disperses the gas sensitive component is sometimes necessary to provide a sufficient contact with gaseous molecules and to obtain an optimum concentration of sensitive material. The matrix should be transparent in the frequency region of interest. A series of silicate glasses is transparent with respect to visible light but doping of a gas sensitive component from the molten state is possible only at high temperatures. With the sol-gel process, however, amorphous silica thin films are easily prepared even at room temperature.[3,4] This method enables to incorporate thermally unstable organic compounds in the pores of the matrix. In the present paper, the optical detection of nitrogen monoxide was developed with a sereis of metal porphine which is dispersed in a silica film with the sol-gel method. Although some sensor materials for NO detection which utilize the resistance change of metal oxides or metal phthalocianines have been reported so far, NO sensors have not been developed satisfactorily at present.

Commercially available α, β, γ, δ-tetrakis (5-sulfothienyl) porphine (Dojindo Laboratries), was used for preparation of its metal complexes, M[T(5-ST)P] (M=Co, Ni, Fe, Cu, Zn, Pb, and H_2). The synthetic procedure consists simply of allowing the porphine and excess divalent metal salt to react in refluxing methanol. M[T(5-ST)P] (3.0×10^{-5} mol) was dissolved in 8 cm^3 of 0.1 mol dm^{-3} aqueous HCl solution. Then, this solution was added to a mixture of ethanol (10 cm^3), ethyl orthosilicate ($Si(OC_2H_5)_4$) (8.0 cm^3), and Triton X-100 (a surface active agent) (1.00 g). After the two solutions were mixed, hydrolysis proceeded slowly at room temperature in the acid catalyzed condition. After aging at room temperature for 24 h, the solution was coated on a glass plate (10 mm × 20 mm × 1 mm) by dipping it in the solution. The amorphous silica films were formed by drying the coated glass plate in air for 7 days at room temperature. Such a slow drying process is necessary to avoid crack formation in the film. Then, the films were evacuated at 200 °C to remove water and ethanol. Sensor performance was tested in a vacuum system by introducing O_2, CO, and NO at 200 °C. The glass plate was placed in a quartz cell with optical windows. Visible spectra were recorded at 200 °C with a Jasco 660 spectrophotometer.



M = Co, Ni, Fe, Cu, Zn, Pb, and H_2

Fig.1. Structure of metal α, β, γ, δ-tetrakis (5-sulfothienyl) porphine, M[T(5-ST)P].

The films coated on both sides of glass plate were about 2 μm in thickness. The BET surface area of the silica matrix was 880 m^2/g, but most of pore diameters were smaller than 6 nm. These pores were large enough to permit adsorption and desorption of small molecules such as O_2, CO, and NO. The amorphous silica matrix was transparent in the wavelength region between 200 and 900 nm and was stable to light irradiation. Among a series of prophine compounds, T(5-ST)P and its metal complexes are soluble in water-ethanol mixture, so that they can be incorporated in amorphous silica matrix by the sol-gel process in a high dispersion state. After heating at 200 °C, M[T(5-ST)P] doped silica film was immersed in 0.1 mol dm^{-3} HCl for a week, but the metal porphine was not detected in the solution. The dopant is sufficiently immobilized in the silica matrix, but its coordination property for gaseous molecules is kept in this state.

M[T(5-ST)P]-amorphous silica films showed a typical band at 430-450 nm (Solet band) due to $\pi \longrightarrow \pi^*$ transition, and the intensity of this band should be changed when molecules are coordinated to the metal. The visible spectra of the films were recorded before and after exposure to O_2, CO, and NO at 200 °C. But the films doped with Fe[T(5-ST)P], Cu[T(5-ST)P], and H_2[T(5-ST)P] exhibited no changes in their visible spectra with introduction of these three gases at 200 °C. The visible bands at 420 - 430 nm of Pb[T(5-ST)P] and Zn[T(5-ST)P] doped films were weakened by a contact with NO, nevertheless the original intensity could not be recovered by evacuation of NO. The response to O_2 or CO was negligibly small on Pb[T(5-ST)P] and on Zn[T(5-ST)P]. The band at 422 nm of Ni[T(5-ST)P] was slightly sensitive to NO; however the decrease in absorbance was only 0.6% with 1.3 × 10^2 Pa of NO. This film was not sensitive to O_2 or CO. The change in absorbance of band centered at 420 nm of Co[T(5-ST)P] was very large when it is exposed to NO, as shown in Fig. 2. When the film was exposed to 1.3 × 10^2 Pa of NO, this band was weakened to about 80% of the original intensity. While the visible band of Co[T(5-ST)P] was very sensitive to coordination of NO, its absorbance was unchanged by an exposure to CO or O_2. Thus, the sensor performance of Co[T(5-ST)P] was studied in detail.

The film doped with Co[T(5-ST)P] had a band centered at 440 nm before heating at 200 °C. However, this band is weakened during pretreatment at 200 °C in vacuo, and then a new band grew at 420 nm. After 1 h, the original band disappeared, being replaced completely with the new band. This spectral change appears to resulted from elimination of water and ethanol, which were contained in the silica film during the preparation procedure. With the heat treatment at 200 °C, the sensitivity of Co[T(5-ST)P] to NO was intensified. As shown in Fig. 2, the spectral change became large with increasing pressure of NO. The original spectrum was completely recovered by evacuating NO at the same temperature. These changes are attributed to the reversible coordination of NO on Co metal.

Figure 3 shows the depencence of the absorbance at 420 nm on NO

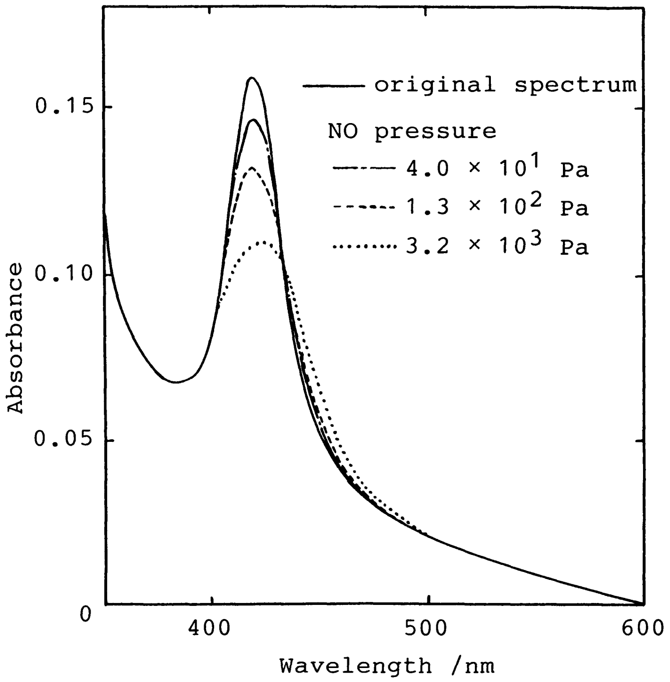


Fig.2. Absorbance spectra of Co[T(5-ST)P] doped film before and after exposure to NO at 200 °C.

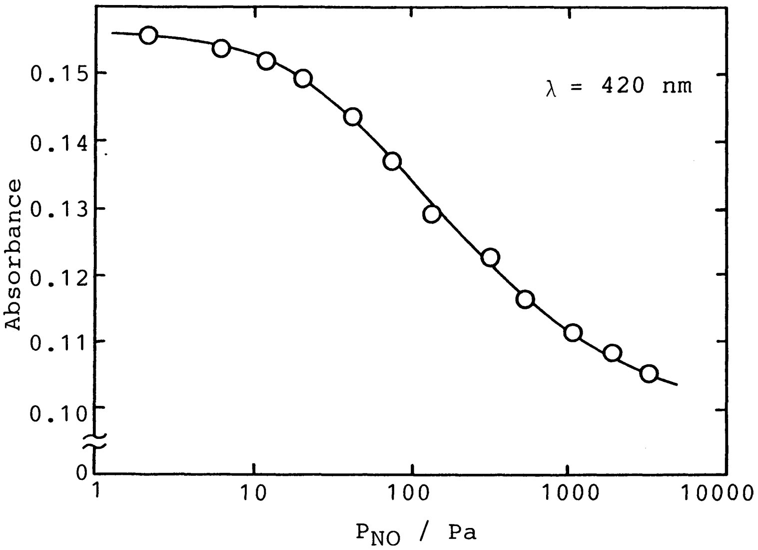


Fig.3. Dependence of the absorbance of Co[T(5-ST)P] doped film on pressure of NO at 200 °C.

pressure at 200 °C. The absorbance decreased with increasing NO pressure in the range of 1.3 to 3.2×10^3 Pa. Below 5 Pa the pressure dependence was small, but it became great above 10 Pa. The absorbance change was about 1% at 1.3 Pa of NO and about 30% at 1.3×10^3 Pa. These change was large enough to detect the concentration of NO by usual spectrometers.

Figure 4 shows the response curves of the sensor with introduction and evacuation of NO at 200 °C. With introducing NO, absorbance decreased quickly and attaind steady value within 20 s. With evacuation of NO, the absorbance increased and was completely restored to the original level within 20 s at 1.7 Pa of NO. Although the recovery time was prolonged with increasing NO pressure, only 60 s was necessary from 1.7×10^2 Pa of NO. Therefore the Co[T(5-ST)P]-doped film had the short response and recovery periods for detection of NO.

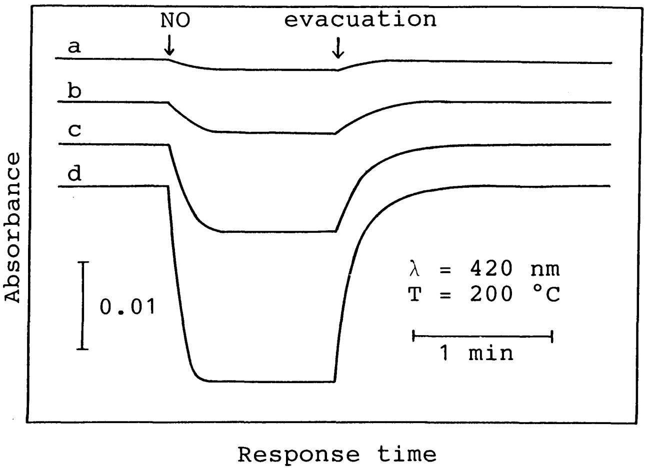


Fig.4. The response curves of the absorbance of Co[T(5-ST)P] doped film, followed by a step change in NO pressure to (a) 1.7 Pa, (b) 8.0 Pa, (c) 67 Pa and (d) 170 Pa and by evacuation.

Since the Co[T(5-ST)P] doped amorphous silica film, which was prepared by sol-gel method, was very effective for optical detection of gaseous NO. The sensitivity of the absorbance at 420 nm, the wide detection range (1.3 - 3.2×10^3 Pa), and the response time were satisfactory to know the concentration of NO by visible spectroscopy. The film was insensitive to CO or O_2. These prominent property of the Co[T(5-ST)P]-amorphous silica film suggests the suitability of this material for an optical fiber sensor.

References

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(Received January 7, 1988)