CHEMISTRY LETTERS, pp. 1995-1998, 1990.

Highly Sensitive Analysis of SnO_2/Solution Interface by Internal Reflection-Fluorescence Spectroscopy

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Internal reflection-fluorescence spectroscopy was applied to the analysis of SnO_2/solution interface. Changes in the fluorescence intensity of 1,3-di-n-butyl-5-[4-[3,3-dimethyl-1-(-sulfopropyl)-2-indolinylidene]-2-butenylidene]-2-thiobarbituric acid sodium salt were measured at very low dye concentration as a function of pH. The point of zero charge and the distribution of the positive charge sites of SnO_2 thin film surface were investigated. The electrochemical potential of SnO_2/solution interface was estimated.

Fluorescence spectroscopy has been applied to obtain microscopic environment information on the dye, since high sensitivity and selection of wavelength of the fluorescent dye. The fluorescence decay of dye at semiconductor/solution interface has been investigated by using a thin layer cell.[1] Internal reflection spectroscopy has been applied to measure the absorbance of adsorbed dyes on the electrode in situ.[2] The internal reflection-fluorescence spectroscopy has been used to determine the concentration-distance profile of an interfacially adsorbed fluorescent protein layer.[3]

At very low ionic dye concentration, more sensitive information about the semiconductor/solution interface can be obtained from fluorescence spectroscopy by using the internal reflection than by using a thin layer cell configuration.

1,3-Di-n-butyl-5-[4-[3,3-dimethyl-1-(-sulfopropyl)-2-indolinylidene]-2-butenylidene]-2-thiobarbituric acid sodium salt (**1**) was supplied by Nippon Kankoh-shikiso Kenkyusho. The solution was prepared from the Britton Robinson buffer solution: a mixture of 0.04 M(1 M= 1 mol dm^{-3}) mixed acids (H_3PO_4+CH_3COOH+H_3BO_3) and 0.2 M NaOH, and **1**. **1** was added immediately before fluorescence measurement to the buffer solution at a concentration varying from 10^{-7} to 10^{-8} M. SnO_2-coated glass plates were supplied by Central Glass.

The fluorescence measurement of the adsorbed **1** at the semiconductor/solution interface from the solution should satisfy the following conditions. First, we should excite not the solution but the semiconductor/solution interface. Second, the fluorescence of the glass plate should be weaker than that of **1**. Third, the cell should be fixed at the same position when the solution is flowed in and out. Thus, a cell such as the one shown in Fig. 1 should satisfy these requirements.

The incident beam of xenon arc lamp (wavelength 550 nm) was introduced into the cutting side of glass plate. The adsorbed **1** at the semiconductor/solution interface was excited by the reflected beam in the glass plate. The fluorescence intensity of **1** at 610 nm was measured using a fluorescencespectrometer Hitachi MPF-4. When the 550 nm excitation wavelength was used, some weak fluorescence of the glass plate was still detectable. Hence, the difference between the fluorescence intensity of the semiconductor/solution interface with and without **1** is taken as the fluorescence intensity of **1** at the semiconductor/solution interface.

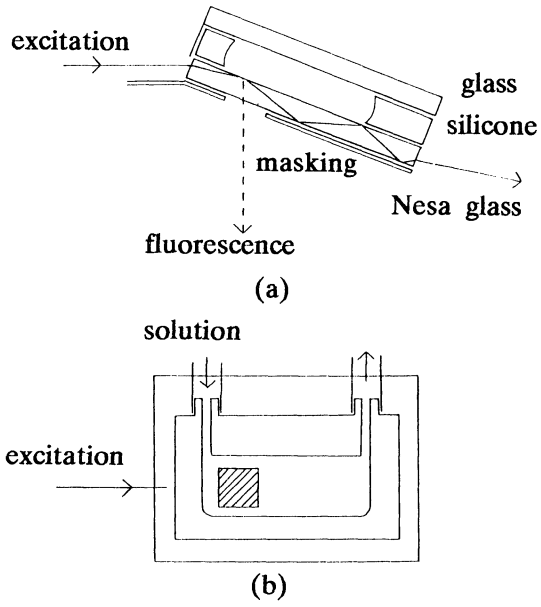

Fig.1. Internal reflection-flourescence cell. (a) Top view. (b) Side view.

Figure 2(a) shows the fluorescence spectrum of adsorbed **1** at the SnO_2/solution interface with the 550 nm excitation. This spectrum shifted by about 5 nm toward longer wavelengths compared with the spectrum of **1** in solution. Figure 2(b) shows the fluorescence intensity (I_{fl}) of **1** at 610 nm observed as functions of time and pH of the solution using the cell shown in Fig. 1.

For solution of pH 6.8, the fluorescence intensity was constant after the addition of the solution in the internal reflection-fluorescence cell. After about 10 minutes, the solution was removed from the cell. The cell was then washed 3 times with the buffer solution. The fluorescence intensity was decreased for each washing. This shows that adsorbed **1** was removed during washing. For solution of pH 5.0, the fluorescence intensity was increased gradually. After 14 minutes, the intensity was also decreased by washing the cell with the buffer solution. After 4 washings, it still had a small value which

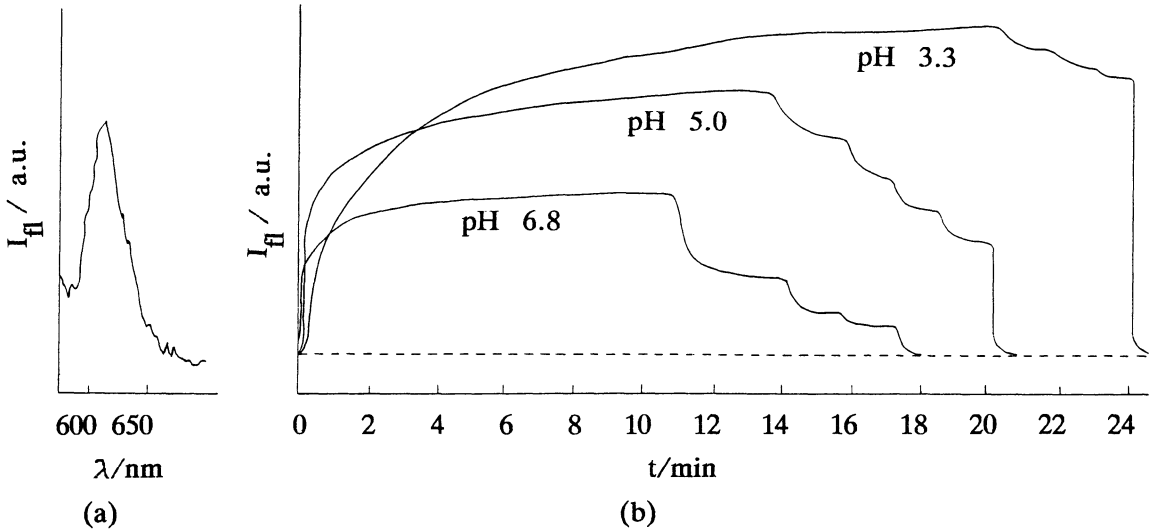

Fig.2. Fluorescence intensity of **1** at SnO_2/solution interface at a dye concentration of 7.0×10^{-8} M with excitation at 550 nm. (a) Fluorescence spectrum. (b) Time dependence at pH 6.8, 5.0, and 3.3.

immediately disappeared by washing the cell with an alcohol. For solution of pH 3.3, a larger fluorescence intensity was observed but it was little affected by washing the cell with the buffer solution. The fluorescence showed a large increase with time for solutions of pH ‹ 5.7 and at a dye concentration of 10^{-7} - 10^{-8} M. This behavior was not observed on an ordinary glass plate.

The fluorescence intensity can be used to indicate the quantity of adsorbed dyes at SnO_2/solution interface. An increase in the fluorescence intensity indicates an increase in the quantity of adsorbed dyes at SnO_2/solution interface. The increase of adsorbed dyes is represented by an electrostatic interaction between the anionic dye and the positive sites of SnO_2 surface. Below pH value of the point of zero charge (pzc) of SnO_2, the SnO_2 surface forms positive sites which are adsorbed by anionic ions through electrostatic interaction. The anionic dyes are adsorbed on the SnO_2 surface from solution below pH value of pzc of SnO_2. By the internal reflection-fluorescence spectroscopy, we could observe the time dependence of the adsorption change of anionic dyes on SnO_2 surface from solution at a very low dye concentration. Such could not be observed by the thin layer cell method of Liang et al.[1] The internal reflection-fluorescence spectroscopy is highly sensitive and it is a useful method for the study of the oxide semiconductor/solution interface.

In Fig. 3, I_{fl} is shown as a function of pH of the solution, after 20 minutes of the addition of the solution to the cell (●) and after washing the cell 3 times with a buffer solution of the same pH (○). For solutions of pH ‹ 5.7, the fluorescence of 1 at SnO_2/solution interface was still observed after washing the cell by a buffer solution. This means that the adsorbed anionic dyes were adsorbed fairly strongly on the SnO_2 surface. For solutions of pH from 5.7 to 4.0, both of the fluorescence intensities at (●) and (○) show similer figure as a function of pH. This means that the distribution of positive sites of SnO_2 surface changes with pH. For solutions of pH ‹ 4.0, the fluorescence intensity was nearly constant, which indicates that the positive sites distribution may be constant. On the other hand, for solutions of pH › 5.7, the fluorescence intensity after 20 minutes was observed at the same value as that immediately after the addition of solution. It was also observed that the fluorescence disappeared after washing the cell with a buffer solution. This indicates that the adsorbed dyes on the SnO_2 surface were washed off by the buffer solution.

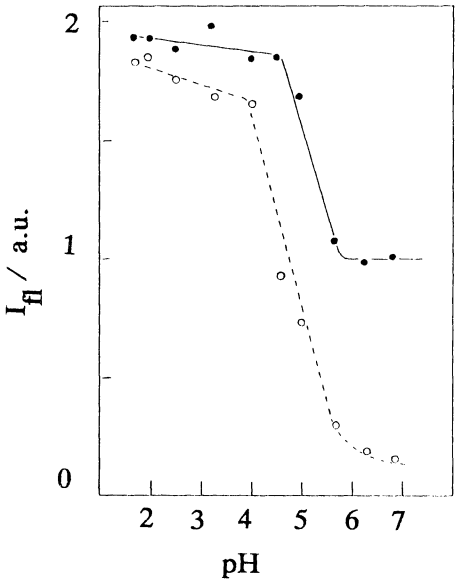

Fig.3. Fluorescence intensity of 1 on SnO_2 glass plate 7.0×10^{-8} M. ●, after 20 minutes ; ○, after washing the cell with a buffer solution only.

The pzc of oxide semiconductor in aqueous suspension has been investigated by electrophoresis method[4,5] and potentiometric titration method.[6-8] The pzc of SnO_2 has been reported to be at pH 4.8 by Lee et al.,[4] pH 4.5 by Johansen et al.[5] and pH 4.3 by Mukai et al.[6] Lee et al. calculated site distributions on oxides and discussed that

there were a small quantity of charge sites at pzc and the positive sites were distributed in the same quantity as the negative sites at pzc.[4] As internal reflection-fluorescence spectroscopy is very sensitive method, the fluorescence intensity after washing the cell (O) may be correlated with the positive sites on SnO_2 surface distribution as a function of pH. From these results, it can be pointed out that the positive sites on SnO_2 surface may be formed at pH ‹ 5.7 and that the positive sites and negative sites coexist at pH range from 5.7 to pzc of SnO_2.

Figure 4 shows the fluorescence intensity after 20 minutes of addition of solution to the cell as a function of dye concentration (c) in the solution. It was observed that the fluorescence intensity increased with an increase in the dye concentration. The resultes in Fig. 4(a) indicate that the adsorption of dyes on SnO_2 surface is well coincident with the Langmuir adsorption isotherm. Then $1/I_{fl}$ was plotted against $c^{-1}\exp(\Delta G/RT)$ using a method similar to that of Kano et al.[9] From the following equation,

$$1/I_{fl}=(1/qN)\{1+(1/ac)\exp(\Delta G/RT)\},$$

the electrochemical potential of SnO_2/solution interface can be estimated when the straight line of the plots of $1/I_{fl}$ against $c^{-1}\exp(\Delta G/RT)$ is coincident with the plotes of $1/I_{fl}$ against $1/c$ at pH 6.8. At pH 6.8, the dye is weakly adsorbed on the neutral sites by nonelectrostatic interaction. From this method, the estimated $-\Delta G$ values were 2.5 kJ mol^{-1} (26 mV) and 2.1 kJ mol^{-1} (22 mV) for pH 2.6 and pH 5.0, respectively.

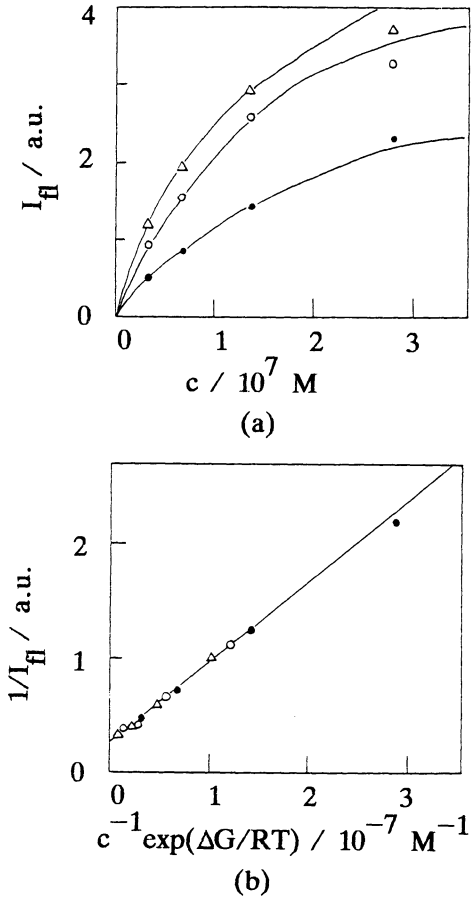

Fig.4. (a) Relation between fluorescence intensity and dye concentration on SnO_2 glass plate. ●,pH 6.8; O,pH 5.0; Δ,pH 2.6. (b) Plots of $1/I_{fl}$ against $c^{-1}\exp(\Delta G/RT)$.

We thank Dr.K.Itoh, Dr.K.Hashimoto, and Dr.B.H.Loo for their helpful discussions.

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(Received July 30, 1990)