Direct Analysis of Dye Molecules on Substrate with Polarized Optical Waveguide Spectroscopy

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Introduction

Optical waveguide (OWG) spectroscopy is a technique based on total internal reflection. OWG spectroscopy is a highly sensitive method of detecting molecules from the absorption of the evanescent wave emerging from the waveguide surface.

We are studying this technique to apply this to electrochemical analysis. OWG spectroscopy is able to analyze the adsorption molecules by using polarized incident light. Two polarized lights were used to detect the direction of molecules as shown in Fig.1. Polarization of incident light was set either to transverse magnetic mode (TM) which is perpendicular to the waveguide and transverse electric mode (TE) which is parallel to the waveguide. When the molecular absorption moment is aligned parallel to the polarized light, the molecules absorb the incident light. For example, Fig.1 (a) molecule absorbs the TM light, but it doesn't absorb the TE light. Similarly, (b) shows absorption but no absorption was found when TM light was used. We can speculate the direction of the absorption moment of molecules on substrate. We call this method "polarized optical waveguide (POW) spectroscopy."

In this study, we discussed dynamic change especially adsorption and aggregation process of methylene blue (MB) molecules on the substrate with POW spectroscopy.

Experimental

MB was purchased from Merck and was used without further purification. Absorption spectra of MB were obtained in the wavelength range 300-700 nm using an OWG spectrophotometer (SIS-50, System Instruments Inc).

As an optical waveguide, a quartz plate (Shin-Etsu Quartz Products, 65 x 20 mm) was used, having thickness 200μm and refractive index 1.46. This OWG plate was suited to analyze the absorption of visible light. The incident light was polarized by a Glan-Thompson polarizing prism placed between the waveguide and the incident optical fiber. The samples prepared on the waveguide were analyzed using two incident polarized light beams (TE and TM polarized light). MB was dissolved in milli-Q water at 4.5mM concentration. This solution was poured directly onto the waveguide (100 $\mu l/cm^2$) and OWG spectra were immediately recorded. For POW spectroscopy, the MB layer was prepared by air-drying of the MB solution on the waveguide. The effect of drying on the molecular state in the cast layer was analyzed dynamically.

Results and Discussion

To discuss orientation of MB and the dynamic adsorption and aggregation process of MB during the air-drying, POW spectra were measured. Fig.2 shows the dynamic change of λ_{max} and the absorbance at the λ_{max} during air-drying. When 4.5mM aqueous solution was poured onto the waveguide, λ_{max} was observed around 600 nm by TM polarized light (Fig. 2 (a)). A slow increase in the absorbance was observed, but the shift of λ_{max} was small. Then, λ_{max} showed a considerable blue shift with an increase in absorbance. The MB solution was concentrated by drying, and some started aggregation. Strong absorption at 545 nm was observed with TM polarized light. This strongly suggested that the MB molecules were highly aggregated, and were standing vertical to the waveguide. When spectral changes were analyzed with TE polarized light, λ_{max} was about 600 nm immediately after pouring the MB solution onto the waveguide similar to the care of TM polarized light. The absorbance at 600 nm increased slowly for a while. This increase was also explained as the concentration of MB molecules at the surface. However, the absorbance was then dropped (Fig. 2). These spectral changes suggested MB molecules were standing vertically to the waveguide and were not excited with TE polarized light.

POW spectroscopy is effective to analyze dynamical aggregation and orientation state of molecules on the waveguide.

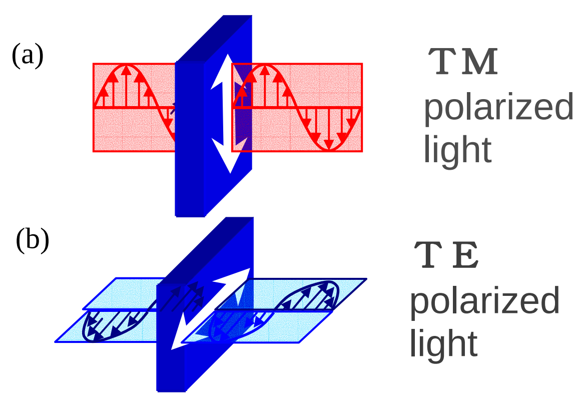

Fig.1 Scheme of TM and TE polarized light and corresponding molecular absorption moment.

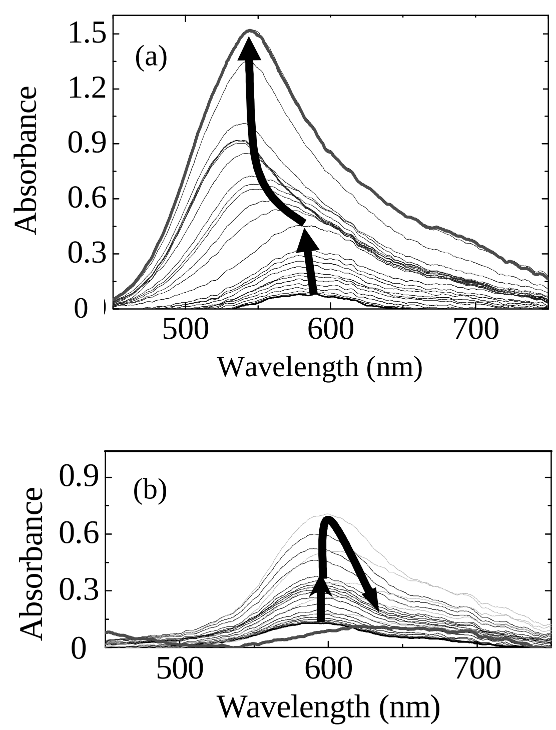

Fig. 2 Dynamic change of OWG spectra during air-drying of MB solution observed by TM (a) and TE (b) polarized light.