In Situ Observation of Adsorbed Heptylviologen Cation Radicals by Slab Optical Waveguide Spectroscopy Utilizing Indium-tin-oxide Electrode

Naoki Matsuda,* Akiko Takatsu, Kenji Kato, and Yuzo Shigesato†

Department of Analytical Chemistry, National Institute of Materials and Chemical Research, AIST, MITI, 1-1, Higashi, Tsukuba 305

†College of Science and Engineering, Aoyama Gakuin University, 6-16-1, Chitosedai, Setagaya-ku, Tokyo 157

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In situ observation of absorption spectra of heptylviologen cation radical ($HV^{+\cdot}$) was performed by slab optical waveguide (SOWG) spectroscopy utilizing indium-tin-oxide (ITO) electrodes. It was found that $HV^{+\cdot}$ existed as both monomer and dimer on ITO with a monolayer deposition. With Nafion coated ITO, a band at about 555 nm disappeared, which indicated that this band was assigned to the adsorbed species consisting of $HV^{+\cdot}$ and the counter anion (Br^-).

In studies of electrochemistry, one of the difficulties to obtain detailed information is caused by the lack of the in situ technique. Recently slab optical waveguide (SOWG) has been applied to devices as optical sensors in chemistry.[1-6] Ito et al observed the change in the reflectance of the interface accompanied by the electrochemical reduction of methylene blue using indium-tin-oxide (ITO) electrode as a SOWG (ITO-SOWG).[7] Saavedra et al also constructed a sensitive ITO-SOWG system.[8] Most research, including the above mentioned ones, has been carried out by a fixed wavelength. However, it is essential to observe absorption spectra of adsorbed materials on electrode because there are possibilities of the existence of multiple bands and the spectral change due to adsorption. The present authors have developed a novel technique using SOWG, with which absorption spectra of adsorbed materials were observed to determine the adsorbed species.[9,10]

Heptylviologen has been well known as one of the candidates of materials for the electrochromic display element, and many studies have been done by electrochemical and spectroscopic methods.[11-13] The solution of HV^{2+} is colorless in the visible region. One-electron reduction step of HV^{2+} resulted in heptylviologen cation radical ($HV^{+\cdot}$), which immediately follows chemical reaction with Br^- and which produced a deposition film on electrodes with strong violet color. It is of much importance to investigate the adsorbed states and electrochemical behavior of $HV^{+\cdot}$. In this study, we obtained the absorption spectra of $HV^{+\cdot}$ adsorbed on the electrode surfaces by ITO-SOWG under electrochemical condition. Additionally, Nafion, cation exchange membrane, was employed to investigate the existence of the adsorbed species composed of $HV^{+\cdot}$ and the counter anion (Br^-).

ITO films were deposited on SiO_2 coated soda-lime glass substrates at Ts=400 ℃ by d.c. magnetron sputtering using a sintered ITO ceramic target containing 10 wt% SnO_2. The sputtering was carried out in a gas mixture of Ar and 0.8 % oxygen under a total gas pressure of 0.13 Pa. A cathode d.c. voltage was kept at 500 V. The residual water vapor pressure was maintained below 10^{-3} Pa (as determined by a quadrupole mass spectrometer) since a low residual water concentration has been shown to improve the reproducibility of film properties. The thickness and resistivity of SnO_2 layer were estimated to be 210 nm and 1.86×10^{-4} Ω·cm, respectively.[14]

The SOWG system was similar to that described previously.[10] The cell length was about 1.5 cm and the surface area of ITO-SOWG covered with sample solution was about 3 cm^2. The electrode potential was controlled with a potentiostat (Hokuto Denko, HAB-151). Counter and reference electrodes were Pt wire and Ag/AgCl, respectively. The electrolyte solution was 0.3 M KBr solution. 1,1`-di-n-heptyl-4,4`-bipyridinium dibromide ($HVBr_2$, generally known as heptylviologen) and KBr were reagent grade, which were purchased from Tokyo Kasei Industry Co. Ltd. and used as received. The sample solution was prepared with distilled water and was deoxygenated with nitrogen gas. The concentration of the sample solution was 25 μM. Transmission absorption spectrum of $HV^{+\cdot}$ adsorbed on ITO electrode was measured by Shimadzu UV-2100PC spectrophotometer with a 1 cm cell. A 5 wt% Nafion solution (Nafion is a registered trademark of Du Pont, Wilmington, DE, USA) was purchased from Aldrich Chemical Co. Inc. The thickness of the Nafion

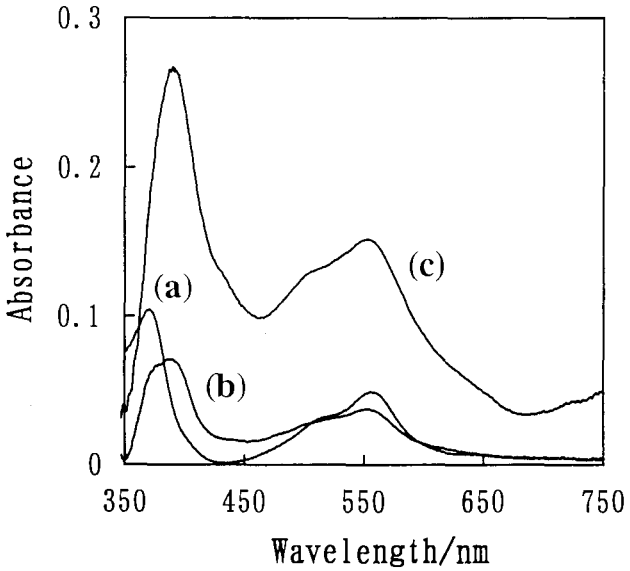

Figure 1. Absorption spectra of heptylviologen cation radical on indium-tin-oxide electrode in 0.3 M KBr solution. (a) was obtained by a transmission absorption spectrophotometer. (b) and (c) were obtained by slab optical waveguide technique. The concentration of heptylviologen was 25 μM. The electrode potential was held at -0.65 V vs Ag/AgCl. (a) and (c) were obtained 5 min after the electrode potential was set at -0.65 V vs Ag/AgCl. (b) was obtained soon after the potential was set at -0.65 V vs Ag/AgCl.

film on ITO electrode was about 4 μm.

Transmission absorption spectrum of $HV^{+\cdot}$ on ITO electrode was shown in Figure 1 (a). The electrode potential was set at -0.65 V. The results corresponded with those obtained by Bewick et al,[11] and two bands at about 370 and 555 nm and a shoulder at about 510 nm were observed. These two bands at 370 and 555 nm have been assigned to dimer of $HV^{+\cdot}$.[12]

Figure 1 (b) and (c) shows the absorption spectra obtained by ITO-SOWG. At first, the electrode potential was held at 0 V and the back ground spectrum was obtained. Then, the electrode potential was scanned at a rate of 50 mV/s and held at -0.65 V to generate $HV^{+\cdot}$. Figure 1 (b) and (c) were obtained soon after and 5 min after the electrode potential set at -0.65 V, respectively. Two bands at about 390 and 555 nm and a shoulder at about 510 nm were observed. These two bands at about 390 and 555 nm have been assigned to monomer and dimer of $HV^{+\cdot}$, respectively.[12] It was shown that both monomer and dimer of $HV^{+\cdot}$ were adsorbed on ITO electrode. As shown in Figure 1(b), at the beginning of the deposition of $HV^{+\cdot}$, a shoulder at about 370 nm was observed.

After the electrode potential was reversed to 0 V, the bands in the spectra disappeared completely. These results indicated that the absorption spectra were attributable to the adsorbed species resulted from the redox reaction of HV^{2+}.

The charge density used for the reduction of HV^{2+} can be estimated from the integration of the reoxidation wave recorded on the cyclic voltammograms. They were 390, 23, and 63 $\mu C/cm^2$ in Figure 1 (a), (b), and (c), respectively. Assuming that one molecule occupies 50 or 100 $Å^2$, charge density necessary for the reduction of $HV^{+\cdot}$ of monolayer coverage is about 32 or 16 $\mu C/cm^2$. In Figure 1(b), $HV^{+\cdot}$ is adsorbed on ITO electrode with about monolayer coverage.

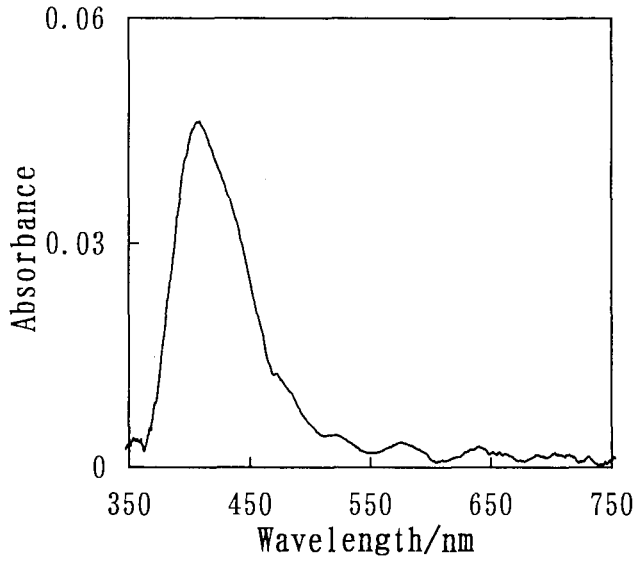

Figure 2. Absorption spectrum of heptylviologen cation radical on Nafion coated indium-tin-oxide electrode using slab optical waveguide in 0.3 M KBr solution. The concentration of heptylviologen was 25 μM. The electrode potential was held at -0.65 V vs Ag/AgCl. The spectrum was obtained 2 hours after the electrode potential set. The thickness of the Nafion film was about 4 μm.

The interaction between $HV^{+\cdot}$ and counter anion has been discussed because it is well known that the adsorbed species and structure of $HV^{+\cdot}$ largely depends on the counter anion. To elucidate the absorption bands assignable to the species consisting of $HV^{+\cdot}$ and Br^-, Nafion film on ITO electrode was employed. Figure 2 shows the absorption spectrum of $HV^{+\cdot}$ adsorbed on Nafion coated ITO electrode using SOWG. The spectrum was obtained 2 hours after the electrode potential was set at -0.65 V. Only one broad band at about 400 nm was observed, and a band at around 555 nm disappeared. Because Nafion film is cation exchange membrane, Br^- can not enter into the film. HV^{2+} can penetrate Nafion film to ITO electrode. Therefore, $HV^{+\cdot}$ can be generated without Br^- by electrochemical reduction inside the Nafion film. These results suggested that the band at 555 nm was assignable to the adsorbed species consisting of the dimer of $HV^{+\cdot}$ and Br^-.

This in situ observation method can give us novel information about adsorption behavior in redox reactions on electrode/electrolyte interfaces. Further investigation is now in progress.

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