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Surface-Enhanced Infrared and Raman Studies of Electrochemical Reduction of Self-Assembled Monolayers Formed from p-Nitrohiophenol at Silver

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The electrochemical reduction of self-assembled monolayers formed from p-nitrothiophenol has been studied *in situ* by surface-enhanced infrared (IR) absorption and Raman scattering (SEIRA and SERS, respectively) spectroscopies. The sensitivity of SEIRA spectroscopy is 20 times higher than that of IR reflection-absorption (IR-RAS) spectroscopy. Combined use of SEIRA and SERS spectroscopies is useful for detailed analyses of electrode reactions and vibrational properties of adsorbed molecules.

Compact monolayers are spontaneously formed when some thiols, carboxylic acids, and silanes are adsorbed on metal surfaces.1) The self-assembled monolayers are of interest for many applications including electrode modification.2) Characterization of these monolayers is required for their wide-spread applications.

Self-assembled monolayers of thiols have been studied with many analytical methods, including IR-RAS,3) SERS,1,4) and electron energy loss spectroscopy (EELS).5) Among these analytical tools, SERS is superior to IR-RAS in sensitivity and to EELS in spectral resolution. Furthermore, SERS is the most suitable tool for *in situ* observation of surfaces in electrochemical environments because glass cells can be used and Raman intensity of water is weak. However, the mechanism of SERS is still unclear6) and, therefore, care must be taken in analyses of SERS spectra.

Recently, SEIRA spectroscopy has been developed as a new surface analytical technique.7-11) SEIRA is a phenomenon that IR absorption of molecules adsorbed on very thin films of free electron metals such as silver, gold, and copper are enhanced greatly (10^1-10^3 times). The SEIRA spectroscopy using Kretchmann attenuated-total-reflection (ATR) configuration enables us *in situ* observation of submonolayers at electrode surfaces in better signal-to-noise ratios and with less interference by electrolytes than IR-RAS.8) In this letter, SERS and SEIRA spectra of self-assembled monolayers formed from p-nitrothiophenol ($HSC_6H_4NO_2$) and p-amino-thiophenol ($HSC_6H_4NH_2$) at silver electrodes are compared. We show that the combined use of SERS and SEIRA spectroscopies is effective for detailed analysis of vibrational properties of the monolayers. Orientations of the monolayers are also described.

A silver rod (5 mm in diameter) embedded in a Teflon rod was used as an electrode for electrochemical and Raman experiments. The electrode was polished to a mirror finish with 0.06-μm alumina particles and sonicated in distilled water. The polished electrode was soaked in an aqueous solution containing 1x10^{-5} M(=mol/dm^3) p-nitro- or p-amino-thiophenol for 10 min. and then sonicated in water to remove the excess molecules from the electrode surface. Oxidation-reduction-cycle treatment of the electrode surface, which is frequently used to observe strong SERS,6) was not carried out in the present study. All the chemicals were regent grade and were used as received. Electrolyte solution was prepared with triply distilled water and was deoxygenated with nitrogen.

Electrochemical and SERS measurements were conducted with a conventional three-compartment glass cell with a platinum counter electrode and a saturated calomel electrode (SCE). The electrode potential was controlled with a potentiostat (Hokuto Denko, HAB-151). The excitation light from a He-Ne laser (NEC, GLG5800) was focused onto the electrode surface through the bottom window of the cell. The Raman scattered light was collected with achromatic lenses, and was analyzed with a triple spectrometer (JASCO, TRS-300) equipped with an image-intensified photo-diode array detector system (Hamamatsu Photonics, M2492, M2493, and C2491).

SEIRA spectra were recorded on a FT-IR spectrometer (JEOL, JIR-100) by use of the cell shown in Fig. 1. The working electrode was a thin (≈20 nm) silver film evaporated on a Ge prism in vacuum. P-polarized infrared beam was introduced through the prism at an incident angle of 60° (Kretchmann ATR configuration).

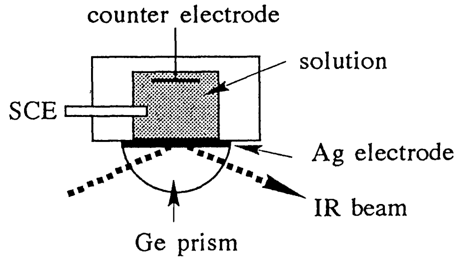

Fig. 1. Electrochemical cell for SEIRA spectroscopy.

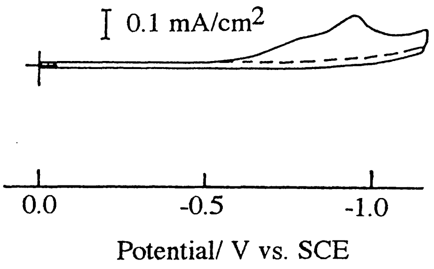

Fig. 2. Cyclic voltammogram of a Ag electrode modified with p-nitothiophenol in 0.1 M $NaClO_4$. Scan rate: 50 mV/s. The dashed trace is for the second scan.

Figure 2 shows a typical cyclic voltammogram of p-nitrothiophenol adsorbed on silver in 0.1 M $NaClO_4$ aqueous solution. A reduction wave is observed around -0.9 V for the cathodic scan. Corresponding oxidation peak is not observed for the anodic scan. No peaks are observed for the second and further scans as shown by the dashed trace in the figure. If it is assumed that the NO_2 group is reduced to NH_2 by a six-electron reduction process, the amount of adsorbed p-nitrothiophenol is calculated to be 6.7×10^{-10} mol/cm^2 from the area under the reduction wave in Fig. 2. This value is comparable with that for the self-assembled monolayer of 2,5-dihydroxythiophenol on gold.3,5)

We show the SEIRA spectrum of the electrode modified with p-nitrothiophenol measured at -1.0 V by subtracting the spectrum at -0.2 V to eliminate the background absorption of water. The peak intensities were 20 times latrger than those in IR-RAS spectrum. The negative-going band at 1346 cm^{-1} assigned to the symmetric NO_2 stretching mode, $\nu_s(NO_2)$, and the positive-going band at 1628 cm^{-1} assigned to the NH_2 deformation mode, $\delta(NH_2)$, demonstrate clearly that the NO_2 group is reduced to NH_2. The SEIRA spectra of the electrode before and after the reductions

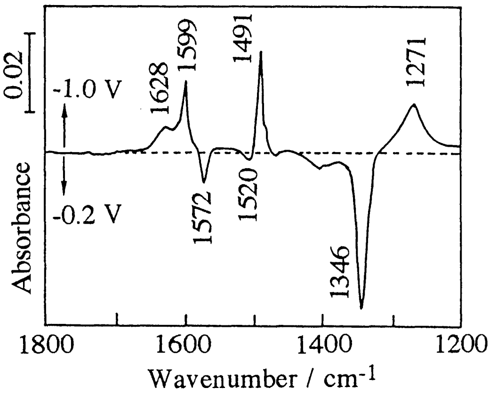

Fig. 3. Potential difference SEIRA spectrum for the reduction of a self-assembled monolayer of p-nitrothiophenol at Ag electrode.

were almost the same as the normal IR spectra of p-nitro- and p-amino-thiophenol (KBr disks), respectively, except the following three differences. First, no SH stretching bands were observed around 2550 cm^{-1} in the SEIRA spectra (and in SERS spectra), indicating that these molecules absorb on the metal surface through the SH groups and dissociates their protons. Second, peak frequencies were slightly (less than 10 cm^{-1}) shifted due to the adsorption. Finally, the anti-symmetric NO_2 stretching band of p-nitrothiophenol, which is strong in the normal IR spectrum, is very weak in the SEIRA spectrum (negative-going band at 1520 cm^{-1}). The difference in relative intensities arises from the selection rule of SEIRA that the vibration modes having oscillating dipoles normal to the metal surface are selectively enhanced.[12)] On the basis of the selection rule, we conclude that p-nitrothiophenol is standing with the phenyl-NO_2 bond nearly normal to the surface. It is also the case for p-aminothiophenol because the vibrations having oscillating dipoles along the phenyl-NH_2 bond (δ(NH_2) and the phenyl-NH_2 stretching mode at 1271 cm^{-1}) are observed strongly. It has been suggested that hydroxyamino-, nitroso-, and azo-compounds are formed during the reduction of nitro-compounds.[13)] However, no characteristic bands of these compounds were observed.

Figure 4 shows the SERS spectra of silver electrode modified with p-nitrothiophenol. The spectra were obtained by synchronizing with the cycling voltammetry in Fig. 2. The excitation source was the 632.8 nm line from the He-Ne laser (10 mW at the sample point). Since the integration time of the detector was 1 s and the potential scan rate was 50 mV/s , the spectrum at a potential E is the averaged one between E and E+0.05 V. The strong ν_s(NO_2) band at 1334 cm^{-1} disappears around -0.7 V for the cathodic scan where the reduction current flows. In the reverse potential scan, several new bands appear at 1436, 1391, and 1142 cm^{-1}.

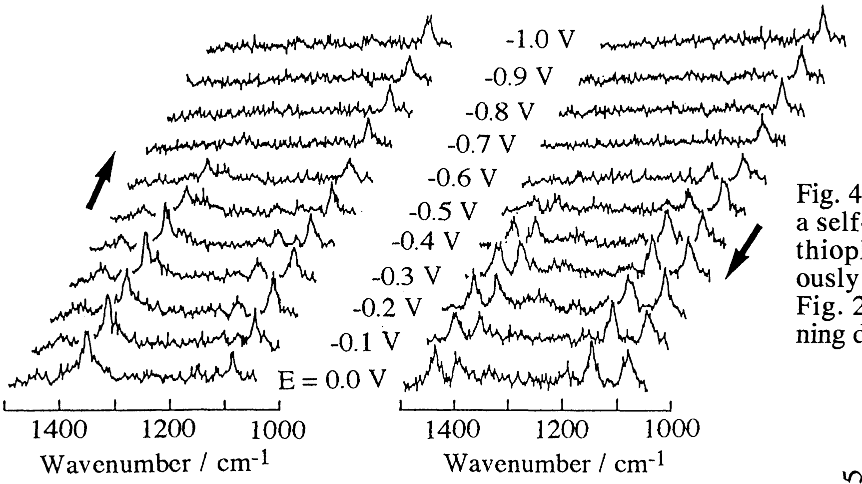

Fig. 4. SERS spectra for the reduction of a self-assembled monolayer of p-nitrothiophenol at Ag obtained simultaneously with the cyclic voltammogram in Fig. 2. The arrows indicate the scanning direction of electrode potential .

The SERS spectrum measured after the reduction is the same as that of the self-assembled monolayer formed from p-aminothiophenol shown in Fig. 5 (solid trace). We note, however, that the SERS spectrum is significantly different from the normal Raman spectrum of the mother compound (powder, dashed trace in Fig. 5). Most SERS bands have their counterparts in the normal Raman spectrum. However, the relative intensities are different greatly. In addition, the peak shifts by the adsorption are 15-30 cm^{-1} and are much larger than those observed in SEIRA spectrum (less than 10 cm^{-1}).

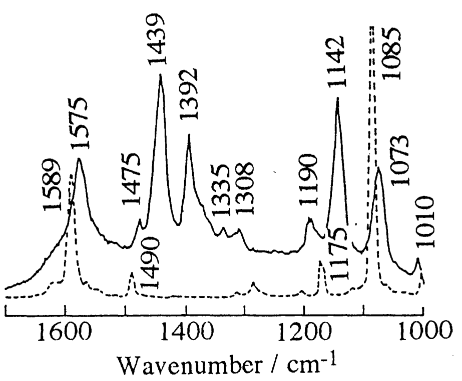

Fig. 5. SERS and normal Raman spectra of p-aminothiophenol (solid and dashed traces, respectively). The SERS spectrum was obtained in the air.

We also note a strange SERS behavior that no spectral features are observed at E<-0.7 V in Fig. 4 except the 1075 cm^{-1} band probably assigned to the breathing mode of phenyl ring. The strong bands reversibly disappeared and re-appeared around -0.7 V for the second and further potential scans.

It is well established that SERS originates from several mechanisms$^{6)}$. Enhancement of Raman intensity associated with the charge transfer (CT) between metal and molecule is one of the most important mechanism. We found that the potential where strong SERS bands of p-aminothiophenol appear and disappear (cf., Fig. 4) shifts to more positive potentials as the Raman excitation energy increases (at a rate of $\approx$1 V/eV). This results strongly suggests the contribution of the CT mechanism to the SERS.$^{14)}$ Since SERS by the CT mechanism is a kind of resonance Raman effect, there is a possibility that some special Raman bands are selectively enhanced$^{6)}$. We think that the remarkable difference between the SERS and normal Raman spectra of p-aminothiophenol arises from the CT mechanism.

In summery, SERS is very useful technique for *in situ* and real-time observation of electrode/electrolyte interfaces. However, the analysis of the spectra is sometimes very difficult when CT mechanism contributes to the enhancement. Therefore, the comparison with IR spectra is very informative for detailed analysis of the vibrational properties of the adsorbed molecules. Although SEIRA spectroscopy can be applied only for thin metal-film electrodes, its high sensitivity allows the comparison of IR spectra with SERS spectra. With use of the Kretchmann ATR technique, we could obtained the spectra of thiol monolayers without interferences by electrolytes and water vapor.

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