

Surface-Assisted Photoinduced Reduction of *p*-Nitrothiophenol Self-Assembled Monolayer Adsorbed on a Smooth Silver Electrode

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It was observed that surface-enhanced Raman scattering (SERS) spectra of *p*-nitrothiophenol (PNTP) self-assembled monolayer adsorbed on a smooth silver electrode changed by laser light irradiation. The SERS spectra were identical with those of *p*-aminothiophenol (PATP). This reaction proceeded even at the electrode potential where PNTP was electrochemically stable under dark. It was found that photoinduced reduction of PNTP occurred on a smooth silver electrode surface.

Surface-enhanced Raman scattering (SERS) has been used to obtain in situ information on electrode/electrolyte interfaces since its first invention in 1974.^{1,4} Additionally, SERS has been known as a powerful tool to study photoinduced surface reaction because of its surface selectivity and sensitivity.⁵⁻⁷ Lombardi and coworkers reported photochemical reduction of *p*-nitrobenzoic acid (PNBA), which has been used as a model compound in SERS studies, on a roughened silver electrode.⁸ We found here that *p*-nitrothiophenol (PNTP) adsorbed on a smooth silver electrode was reduced with laser light irradiation. There are two advantages to investigate photoinduced surface reaction in this system. One is that SERS intensity of PNTP was so strong even on a smooth silver electrode that there was no need of oxidation-reduction cycles (ORC). This enabled us to estimate the dependence of SERS spectra on the electrode potential without the influence of electrode surface transformation induced by cathodic potential sweep. The other is that the intensity of SERS spectra from PNTP did not reduce after cathodic potential sweep even when PNTP was not added to electrolyte solution in the cell. Since there was no interaction between unreacted molecules in the electrolyte solution and reaction products adsorbing on the electrode surface, it was easy to observe SERS spectra from the adsorbing molecules and to determine reaction products. In this letter, we report photoinduced reduction of PNTP self-assembled monolayer films on a smooth silver electrode.

The electrochemical cells, and Raman system used in this study were the same as described previously.⁹ A silver working electrode was polished to a mirror finish with alumina particles (1.0, 0.3, and 0.06 μm) and sonicated in distilled water. The method for preparing PNTP self-assembled monolayer films on silver electrodes has been already described.⁹ Since no ORC treatment was employed in this study, surfaces of silver working electrodes were smooth. Sodium perchlorate was used as a supporting electrolyte. All the chemicals were reagent grade, which were purchased from Kanto Chemical Co. Ltd. and used as received. The electrolyte solution was prepared with triply distilled water and was deoxygenated with nitrogen gas. The 632.8-nm line from a He-Ne of a power of 20 mW at a sample was used as the SERS excitation source. The diameter of the laser beam on a silver electrode was ca. 500 μm . All the electrode potentials were quoted to saturated calomel electrode (SCE).

Figure 1 shows the SERS spectra during the electrochemical reduction measured at an interval of 0.1V from 0 to -0.8V. Before starting each measurement, the electrode potential was being kept constant for 60 seconds, and it took again 60 seconds for a spectrum to be obtained. The first spectrum in Fig. 1 corresponds to that of PNTP, and is characterized by a strong band at 1335 cm^{-1} assigned to the symmetric NO_2 stretching mode, $\nu_s(\text{NO}_2)$. As the electrode potential was swept to the cathodic direction, the bands assigned to PNTP gradually decreased in intensity, and alternatively those assigned to *p*-aminothiophenol (PATP) started to appear. In the 6th spectrum in Fig. 1 at -0.5V the change of the SERS spectrum has already finished, and it almost corresponds to that of PATP. Figure 2 is the SERS spectra of PNTP after giving back the electrode potential to 0V and corresponds to that of PATP. There is a possibility that nitroso-, hydroxyamino-, and azo-compounds are formed during electrochemical

reduction of aromatic nitro compound, but any characteristic band of these compounds was not observed in our experiment.^{8,10,11}

Because the reduction wave started to appear at around -0.6V in CV, the cause by which the reduction of PNTP has been completed at -0.5V as shown in Fig. 1 can't be attributable to the electrochemical reduction. As is reported in our previous paper,⁹ any band assigned to PATP was never observed at -0.5V in the first potential sweep to the cathodic direction when the SERS spectra were obtained by synchronizing with CV on a triangle potential wave form at a scan rate of 50 mV/s. In this experiment, the time interval between two neighboring spectra which were measured at an interval of 0.1V was 2

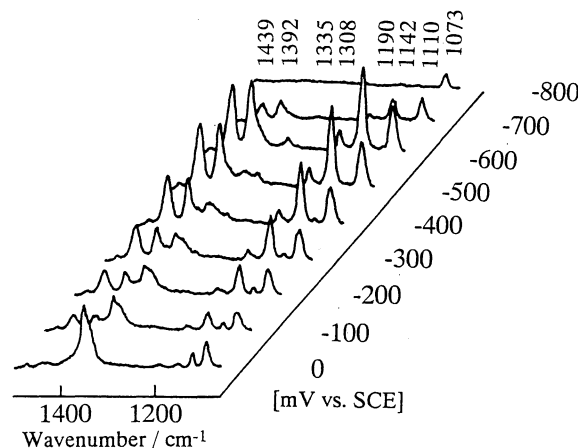


Fig. 1. SERS spectra of *p*-nitrothiophenol at Ag with changing applied potentials, using 20 mW of He-Ne 632.8-nm laser light.

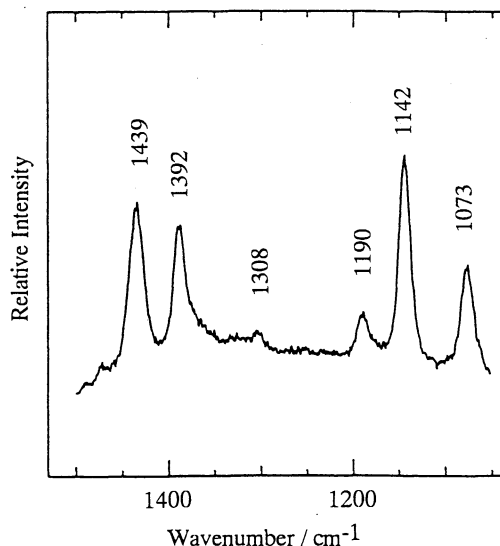


Fig. 2. SERS spectra of *p*-nitrothiophenol at Ag obtained after potential scan, using 20 mW of He-Ne 632.8-nm laser light. The electrode potential was set at 0V vs. SCE.

seconds. Main difference in the experimental conditions between this result and that shown in Fig. 1 was the time duration of laser light irradiation. Therefore it was suggested that the laser light irradiation was the cause of reduction of PNTP to PATP.

Figure 3 shows the time dependence of the SERS spectra, in which the electrode potential was being fixed at 0V. Soon after beginning of laser light irradiation, the SERS spectrum is identical with that of PNTP, the same as the first spectra of Fig. 1 at 0V. As time passing, the bands assigned to PATP increased in intensity instead of those assigned to PNTP. After 160 minutes, the SERS spectrum changes to that of PATP. The change of SERS spectra stopped when the laser light irradiation on PNTP was ceased. In addition, it is observed that the time dependent change of the SERS spectra of PNTP occurred from the beginning whenever the spot of laser light was moved to the other place on a silver electrode. Since the change of SERS spectra was observed even at 0V, it was shown that PNTP adsorbed on a silver electrode was reduced to PATP by laser light.

In addition, there was no observable change in the normal Raman spectra of PNTP in water solution under the same excitation conditions as those in SERS study. Since the photochemical reduction in the solution phase necessitates an excitation by UV light, the photo-induced reduction of PNTP on silver was not a mere photochemical one. These results mentioned above imply that adsorption on a silver surface results in an enhancement of the photoinduced reduction of PNTP. After heating PNTP adsorbed on a silver surface to 150°C for 2 hours in an oven, no change in the SERS spectra was observed in air atmosphere. This indicates that the reduction of PNTP was not a thermal process.

It is well established that charge transfer (CT) mechanism between the Fermi level of a metal electrode and the states of adsorbing molecules caused by direct light absorption is one of the most important mechanisms for SERS along with electromagnetic (EM) mechanism. Lombardi and coworkers conclude that EM mechanism is the main reason in the photolysis of PNBA.⁸ Since in our study a smooth electrode was used, it seems that EM mechanism, which necessitates the surface roughness features constructed by ORC, is not the source of the photoinduced reduction and that CT mechanism contributes to the reaction.

Furthermore, a strange SERS behavior that there was no spectral features except the band at 1075 cm⁻¹ at E = -0.8V in Fig. 1 was observed. When the electrode potential was returned to 0V, the strong SERS spectra assigned to PATP was observed as shown in Fig. 2. After the

potential sweeps between E=0 and -0.8V were repeated several times, SERS intensity was still strong. It has been already reported that thiols including PATP were stable in a potential window of a silver electrode.¹³ Though it is impossible to probe the stability of PNTP on a silver electrode against the cathodic potential sweep, it is concluded that PATP which was a reaction product from PNTP continued to be adsorbed on a silver electrode. We believe that the reason why the SERS spectra disappeared at -0.8V is not the desorption of molecules but the deviation from the tune of CT resonance.¹² This result also strongly suggests the contribution of CT mechanism to this reduction.

As a conclusion, it was found that laser light irradiation induced surface-assisted reduction of PNTP at a potential region where PNTP is stable electrochemically. This reaction proceeded even on a smooth silver electrode which was prepared only by polishing. We have also observed that the same spectral changes of PNTP as shown in Fig. 3 occurred on roughened gold and copper electrodes. From SERS spectra the reaction product is PATP, and further study using IR reflection-absorption spectroscopy is now underway. Investigating the dependence of the reduction rate on the excitation wave length and electrode potential will make it possible to obtain direct evidence of CT mechanism of SERS and surface photoinduced reaction. Moreover detail understanding of the photoinduced reduction of PNTP will be a great help to elucidate the electrochemical reduction of aromatic nitro compound, which is well known to be complex. The use of PNTP self-assembled monolayer on a silver electrode has enabled us to obtain a detailed information about a photoinduced reaction occurring only on electrode/electrolyte interfaces.

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References and Notes

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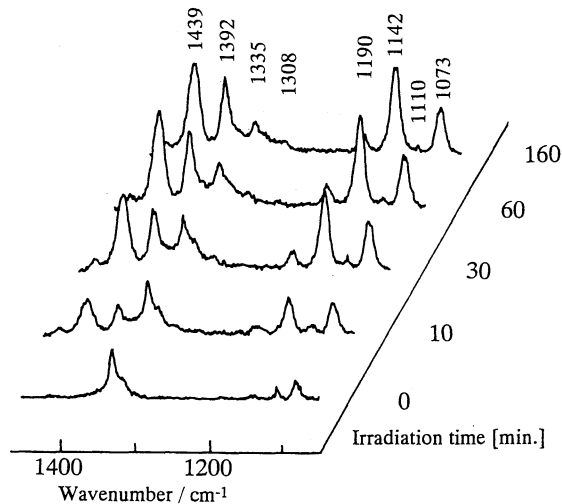


Fig. 3. Irradiation time dependence of SERS spectra of p-nitrothiophenol at Ag with 20 mW of He-Ne 632.8-nm laser light. The electrode potential was set at 0 V vs. SCE.