Photosensitive Oligomer Formation and Laser-induced Polymerization of Aniline on a Gold Electrode Surface: A Surface-Enhanced Raman Scattering Study

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The process of laser-induced electropolymerization of aniline was studied by *in situ* surface-enhanced Raman scattering (SERS) spectroscopy and cyclic voltammetry (CV). Formation of *p*-coupled aniline oligomers was confirmed at an electrode potential below the oxidation potential of aniline, and the oligomers were found to be the source compound for photo-induced electropolymerization.

Self-assembled monolayers and micropatterned monolayers on metal surfaces have attracted much attentions recently,[1-3] because additional chemical functions can be given by the modification of metal surfaces with conducting polymers such as polyaniline, polythiophene and polypyrrole.[4] In the previous study, electropolymerization of aniline was studied by a FT-IR microspectroscopy, and laser-induced electrodeposition of polyaniline on a gold electrode was achieved for the first time.[5] This new synthetic method was demonstrated to produce a micropattern of polyaniline with a μm-order space resolution.[6] The origin and mechanism of the laser-induced electrodeposition, however, have not been clarified. In this communication, we examined the mechanism of photo-induced polymerization of aniline by SERS and CV, and it was found that formation of oligomer is the determining step of laser-induced polymerization.

All chemicals were obtained as reagent grades from Kanto Chemical Co. Inc. Aniline was purified by vacuum distillation twice and stored cold in the dark. All solutions were prepared with water purified by a Milli-Q system (Millipore Corp.). Solutions were deoxygenated prior to each experiment by bubbling argon gas.

The electrochemical cell used was consisted of three electrodes: a working electrode of polycrystalline gold disk (5 mmϕ and 1 mmϕ, Nilaco Corp.), a counter electrode of Pt wire (4.7 cm^2), and a reference electrode of Ag/AgCl/sat.KCl (198 mV *vs.* SHE). A clean gold surface was obtained by polishing with 1 and 0.05 μm alumina slurries, and the polished electrode was annealed in a hydrogen flame. The surface-enhancement was achieved by oxidation-reduction cycles(ORC) in 0.1 mol dm^{-3} KCl solution as described in a literature.[7] Electrode potential was controlled with a potentiostat (Hokutodenko, Model HA-501G) and a function generator (Hokutodenko, Model HB-105). An Ar^+ laser (Lexel Model 95, 514.5 nm, 30 mW) was used as a reaction source of polymerization. The laser beam was aligned coaxially with a Nd:YAG laser (1064 nm, 250 mW), which was used as an excitation source of Raman measurements and assured of no contribution to photo-polymerization. Raman spectra were recorded with a Fourier transform Raman spectrometer (Bruker, IFS 66v).

The voltammetric behavior of aniline was examined with and without irradiation of an Ar^+ laser. Figure 1 shows a cyclic voltammogram of a 0.05 M aqueous aniline solution without irradiation. In Figure 1, the potential region can be divided into three. During the potential from ca. -0.2 V to 0.3 V, the current is almost constant and very small(region I). As the potential rises above 0.3 V, the current increases gradually and a shoulder can be recognized at around 0.4 V (region II). The current increases steeply above 0.5 V(region III). The increase of current above 0.5 V is attributed to oxidation reaction of aniline described in many literatures.[8] This CV feature agrees well with the previous study of neutral aniline solution[8] except for the shoulder appeared in the region II. The shoulder is remarkably recognized if clean electrodes are used, suggesting that the adsorbed species is possibly responsible for the origin of the appearance of the small shoulder.

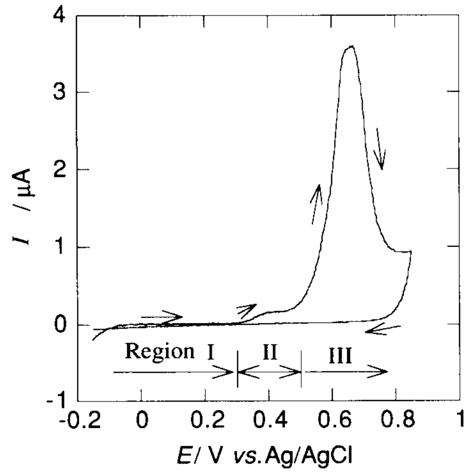

Figure 1. A cyclic voltammogram of a gold electrode in contact with neutral aqueous aniline solution. Sweep rate: 10 mV s^{-1}, 1 mmϕ gold, 0.05 mol dm^{-3} aniline, 0.1 mol dm^{-3} KCl, pH 7.0.

When a laser irradiated the electrode surface, the profile of the voltammogram became remarkably different from the result shown in Figure 1. The difference was recognized in the region II, and a steep increase of current was observed with irradiation. As a result, area-selective polymerization can proceed on the electrode surface. As for the region I, no difference is observed irrespective of irradiation. In the region III, polymerization proceeds irrespective of irradiation. From these facts, it can be said that the species on the electrode surface in the region II is essential for laser-induced electropolymerization.

To elucidate the electrochemical characteristics, dependence of peak current and peak potential on the potential sweep rate was examined in the region II. It was found that both peak current and peak potential were linearly dependent on the sweep rate. These results mean that the chemical species in the region II adsorb on the electrode surface, and that the diffusion of electroactive species from bulk solution to the

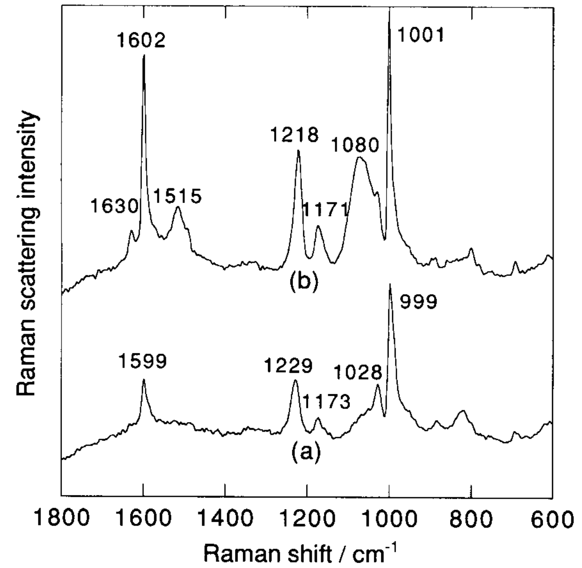

Figure 2. SERS spectra at different electrode potentials without irradiation of Ar^+ laser (a) -0.15 V and (b) 0.40 V *vs.* Ag/AgCl in neutral aqueous aniline solution. 0.05 mol dm^{-3} aniline, 0.1 mol dm^{-3} KCl, pH 7.0. 4 cm^{-1} resolution.

electrode surface does not contribute to the voltammogram. In addition, the electrochemical reaction was found to be irreversible.

Figure 2 shows SERS spectra obtained for a gold electrode immersed in 0.05 M aniline solution at different potentials without irradiation. The bottom spectrum measured at -0.15 V (region I) is almost identical with the result reported by Shindo,[9] and aniline molecules adsorb flatly on the electrode surface without oxidation. The Raman line of C-N stretching vibration is not observed at 1278 cm^{-1}, which is characteristic of neutral aniline in a solution. Thus, it can be disregarded of chemical species in a bulk solution to SERS spectrum. The top spectrum in Figure 2 was measured after the electrode potential was raised from -0.15 V to +0.40 V (region II). The intense Raman lines which appeared at 1001 and 1602 cm^{-1} are characteristics to monosubstituted benzenes, and assigned to ring deformation and C=C stretching vibrational modes, respectively.[10] Comparing the top spectrum with the bottom one, it can be easily recognized that new Raman lines appear at 1630 and 1515 cm^{-1}, which cannot be assigned to aniline monomer. Moreover, the disappearance of C-N stretching vibration at 1229 cm^{-1} and the appearance at 1218 cm^{-1} suggest that aniline no longer exists as monomer at 0.4 V. The spectral feature at 0.4 V is quite similar to that of diphenyl-*p*-phenylenediimine.[11] This similarity suggests that species adsorbed on the electrode surface has quinoid ring structure in the region II, that is, *p*-coupled oligomer of aniline are formed at the electrode surface. When the electrode potential was reversed from 0.4 V to -0.15 V, the SERS spectrum did not show any change. Accordingly, it can be said that aniline oligomers are irreversibly formed at 0.4 V *vs.* Ag/AgCl.

When an Ar^+ laser irradiates the electrode surface at 0.4 V, drastic spectral change occurs as shown at the bottom in Figure 3. By irradiation of an Ar^+ laser, the intensity of Raman lines at 1001 and 1602 cm^{-1} decreases and new Raman lines appear at 1300-1400 cm^{-1} region, which are assigned to delocalized C-N-C stretching vibrational mode characteristic to polyaniline.[12] SERS spectrum of polyaniline is also shown in Figure 3 for comparison, and it corresponds to the bottom spectrum.

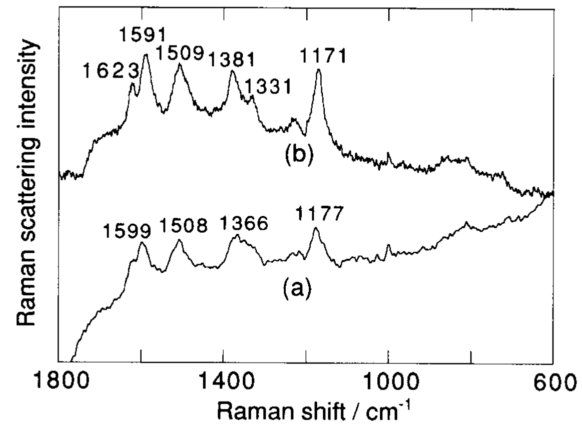

Figure 3. SERS spectra of (a) photo-products after irradiation of Ar^+ laser for 5 min onto gold electrode surface at 0.4 V *vs.* Ag/AgCl and (b) polyaniline formed in the dark at 0.7 V.

From the measurements of CV and SERS, the existence of aniline oligomers is suggested at the electrode potential of ca. 0.4 V. Since diphenyl-*p*-phenylenediimine has visible absorption around 450 nm,[13] it is probable that the aniline oligomers can be excited by an Ar^+ laser(514.5 nm). The excited oligomer would have a lower oxidation potential than aniline monomer and promote subsequent oxidative polymerization.

In conclusion, it is clarified that laser-induced polymerization is caused by an excitation of oligomers produced irreversibly on a gold electrode. The laser-induced polymerization described in this study can be applicable to direct micropatterning of polymers on metal surface in contrast to other methods in which patterning was carried out indirectly using photo-decomposition of self-assembled monolayers.[1-3]

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