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Time-Resolved Near-Infrared Surface-Enhanced Raman Spectroscopy of a Surface-Confined Electrochemical Reaction of 9,10-Phenanthrenequinone

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A measurement system for time-resolved surface-enhanced Raman spectroscopy with a submillisecond time resolution was developed using a step-scan near-infrared Fourier-transform spectrometer and was applied to analyze a redox reaction of 9,10-phenanthrenequinone (PQ) adsorbed on a polycrystalline gold electrode. In the time-resolved surface-enhanced Raman spectra, both quinone and hydroquinone forms of PQ were recognized, but the intermediate species, semiquinone radicals, were not. It was suggested that the lifetime of the intermedeate species was shorter than 0.5 ms, which was the time resolution of the developed system.

Electrochemical processes at electrode surfaces have attracted much attention so far and a variety of measurement techniques have been applied to investigate molecules adsorbed on electrodes.[1] Among the measurement techniques, in situ vibrational spectroscopies[2] have been extensively used, since vibrational spectra directly reflect structural information which cannot be obtained by conventional electroanalytical methods. Various methodologies, such as infrared absorption with a polarization or potential modulation[3] and surface-enhanced Raman scattering (SERS),[4] have been used to eliminate interferences from molecules in a bulk solution and applied in situ to elucidate structural information of molecules at electrode surfaces.

A time-resolved IR technique with a millisecond resolution was first reported by Nakamura et al.[5] using reflection absorption spectroscopy, and was extended to a submillisecond region by Osawa et al.[6] using a surface-enhanced attenuated total reflection technique. As for time-resolved SERS, measurements have been carried out using a dispersive spectrometer equipped with a photon-counting or multichannel detection system. Early studies were reported for the electroreduction of nitro compounds on a time scale of seconds[7] and milliseconds,[8] and Zhang[9] et al. achieved tens of ns resolution on the photoinduced charge transfer of flavin. In all of these time-resolved SERS measurements, a visible laser was used as an excitation source and silver or gold was used as a working electrode. Considering the electrochemical measurements of reactions at electrode surfaces, gold is a more preferable electrode material than silver, since it has a wider anodic potential window than silver. The wide potential window means that a gold electrode is applicable to a variety of compounds. The enhancement factor is large for gold in the near-infrared spectral region, whereas silver shows an enhancement in the visible region.[10] Thus, the combination of near-infrared excitation and a gold electrode is suitable for SERS measurements[11—14] of electrochemical reactions.

Near-infrared excitation is beneficial in spectral measurements because it prevents undesirable photoinduced effects, such as the photodecomposition of samples. However, a major disadvantage of near-infrared excitation for Raman spectroscopy is that near-infrared detectors are less sensitive than visible region detectors. To overcome this disadvantage, Fourier transform (FT) interferometry has been used for Raman measurements in the near-infrared spectral region during the last decade[15] because an FT spectrometer can offer a broad spectral range with high resolution and a fast data-acquisition time originating from multiplex and throughput advantages of FT spectroscopy. Moreover, recent developments of measurement systems using a step-scan mode make it possible to apply FT-Raman to investigate time-dependent phenomena. However, no results for time-resolved Raman spectroscopy by step-scan have yet been reported, except for preliminary results with low spectral resolution.[16]

In the present paper, we first report on submillisecond time-resolved SERS measurements of an electrochemical reaction using a step-scan FT-Raman spectrometer. The developed method was applied to analyze the overall two-electron redox reaction of 9,10-phenanthrenequinone (PQ) adsorbed on a gold electrode. It has been known that PQ adsorbs irreversibly on graphite electrodes in aqueous solutions and shows a surface-confined reversible redox reaction.[17—20] This reaction mechanism has been analyzed by conventional electrochemical methods. However, no spectral measurements have been reported so far. Thus, time-resolved FT-SERS was applied to analyze the electrochemical reaction of PQ.

Experimental

Analytical-grade hydrochloric acid was purchased from Wako Pure Chemical Industries Ltd. (Wako, Osaka, Japan) and used as received. All other chemicals of reagent grade were purchased from Wako and purified according to the following procedures: 9,10-phenanthrenequinone (PQ) was sublimed under vacuum; potassium chloride was recrystallized twice from methanol/water solution; methanol was fractionally distillated. Water was purified by a Milli-Q Labo System (Millipore Corp., Bedford, Massachusetts, U.S.A.) until the resistivity was higher than 18 MΩ cm. All solutions used for electrochemical measurements were prepared with 1 mM (M = mol dm^{-3}) PQ methanolic solution, supporting electrolytes and water. Solutions were deoxygenated by purging with Ar gas (99.998%) for at least 10 min prior to each series of electrochemical measurements. During the electrochemical and spectroelectrochemical measurements, the electrochemical cell was filled with Ar gas to prevent oxygen from dissolving.

The electrochemical cell consisted of a polycrystalline gold electrode (99.9%), a platinum counter electrode, and an Ag/AgCl/sat. KCl electrode as a reference. All potentials described in this paper are quoted vs. Ag/AgCl/sat. KCl. Gold electrodes were successively polished mechanically with two kinds of alumina suspensions (Baikalox®, Baikowski, Annecy, France) having different particle diameters (1.0 μm and 0.05 μm). After polishing, alumina suspensions were completely removed by rinsing with pure water in an ultrasonic bath three times. To obtain SERS activity, the polished-gold electrode was roughened by oxidation–reduction cycles (ORCs). The ORC treatment was done in a 0.1 M KCl aqueous solution by applying a linear potential sweep between 0.05 and 1.25 V with 100 mV s^{-1} for 30 scans; the electrode was washed thoroughly with a 0.1 M KCl solution. For voltammetric measurements, a mechanically polished gold electrode was annealed in an H_2-flame and then immediately immersed into pure water. Electrodes treated with the above procedure gave reproducible cyclic voltammograms.

Cyclic voltammetry experiments were carried out using a potentiostat (HA501G, Hokutodenko, Tokyo, Japan) and a function generator (HB105, Hokutodenko, Tokyo, Japan). Voltammetric data were collected and processed using a personal computer equipped with a 12-bit analog-to-digital converter.

Figure 1 shows the instrumental setup used for SERS and time-resolved SERS measurements. The potential was controlled with a potentiostat (PS-06, Toho Technical Research, Tokyo, Japan) having a response time of less than 10 μs. A square wave (20 Hz) was produced with a function generator (FG-163, NF Electronic Instruments, Yokohama, Japan) and was applied to the electrochemical cell using the potentiostat. SERS measurements were carried out using an FT-Raman spectrometer (IFS-66v, Bruker, Silberstreifen, Germany) equipped with a liquid-nitrogen cooled Ge detector and a diode-pumped Nd : YAG laser (250 mW, 1064 nm, CW). Time-resolved SERS measurements were carried out using a step-scan mode which was synchronized with the delayed trigger produced by a delay/pulse generator (DG535, Stanford Research Systems, Sunnyvale, California, U.S.A.). Asynchronous SERS spectra were also measured with the system shown in Fig. 1. It was confirmed, using a laser diode (λ = 1145 nm), that the detector rise-time was within 0.5 ms for 90% response, and the time resolution of the step-scan spectrometer developed in this study was shorter than 1 ms. The spectrometer was operated at a 4 cm^{-1} spectral resolution. A series of time-resolved SERS spectra were measured within 4 hours at a 20 Hz trigger repetition.

All measurements were carried out at 25±1 °C.

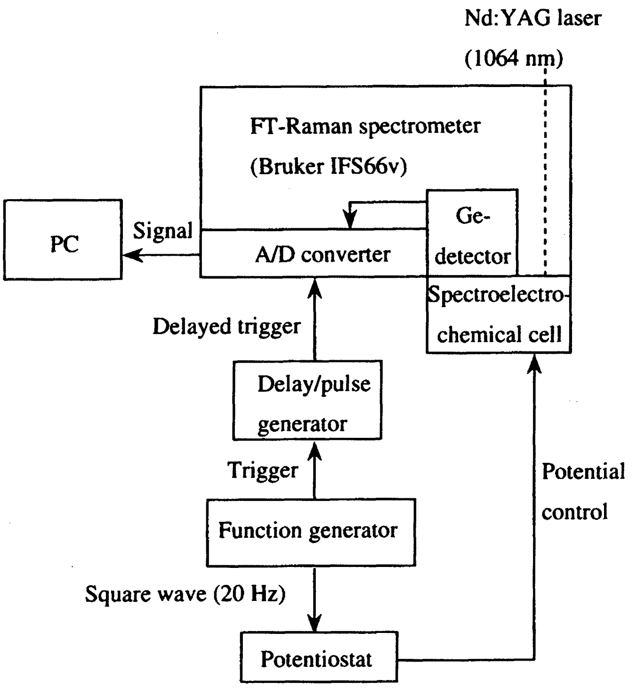

Fig. 1. Schematic diagram of the time-resolved Fourier transform surface-enhanced Raman scattering measurement system.

Results and Discussion

The redox reaction of 9,10-phenanthrenequione (PQ) has been studied using graphite electrodes in aqueous solutions,[17—20] and it has been known that PQ adsorbs irreversibly on graphite elctrodes and shows a surface-confined reversible redox reaction. It is interesting to investigate redox reactions of PQ on a gold electrode, since electrodes used in electrochemical studies of PQ are limited to graphites. The redox reaction of PQ in an acidic solution can be written as Fig. 2. Cyclic voltammograms were measured for an aqueous solution containing 20 μM PQ, 0.4 M KCl and 0.1 M HCl using polycrystalline gold disk as a working electrode. The dependence of sweep rate on the peak current and peak potential of a voltammogram was examined to determine whether electroactive species can be assigned to adsorbed species on the electrode surface[21] or not. The results are shown in Fig. 3. It can be immediately seen from Fig. 3 that both anodic and cathodic waves show peak maxima or minima at approximately the same electrode potential of around 0.22 V. When the peak current was plotted against the sweep rate, a linear relationship was obtained; this result is inserted in Fig. 3. These results indicate that the electroactive species can be assigned to adsorbed species on the gold electrode

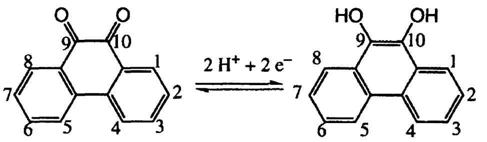

Fig. 2. Structures and electrode reaction in acidic solution of 9,10-phenanthrenequinone.

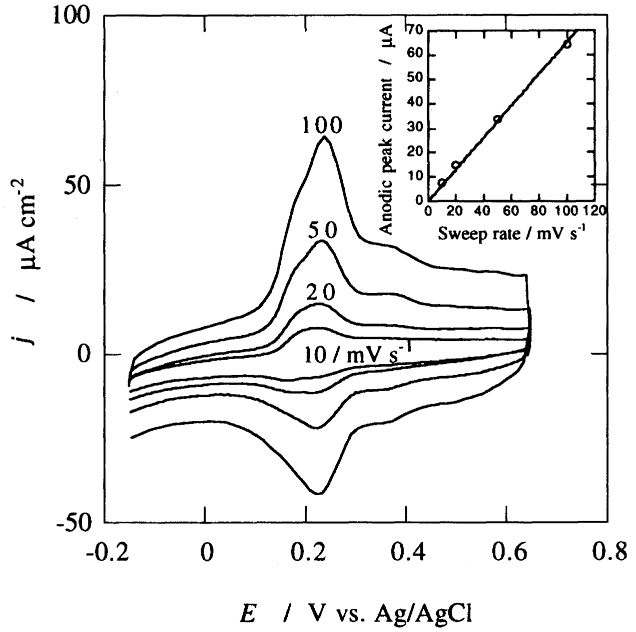

Fig. 3. Sweep rate dependence of the cyclic voltammogram for 9,10-phenanthrenequinone aqueous solution at pH 1.08 using a smooth gold electrode.

similarly to the case of graphite electrodes.

In order to ensure compatibility between electrochemical reactions on roughened and smooth electrode surfaces, cyclic voltammograms were measured using a roughened gold electrode which was used for SERS measurements. The results are shown in Fig. 4, and the peak maxima or minima of anodic or cathodic waves locate at almost a constant potential, indicating the adsorption of the electroactive species to the electrode surface. In addition, a linear relationship was obtained between the peak currents and the sweep rates similarly to the results shown in Fig. 3. As shown in Figs. 3 and 4, it can be recognized that the gold electrode surface roughened for SERS activity gives approximately the same cyclic voltammograms to those obtained by a smooth electrode surface, except for an increase in the current density due to an enlarged surface area produced by the roughening treatment. In accordance with this compatibility, the electrochemical behaviors of PQ on a gold electrode were investigated by SERS measurements.

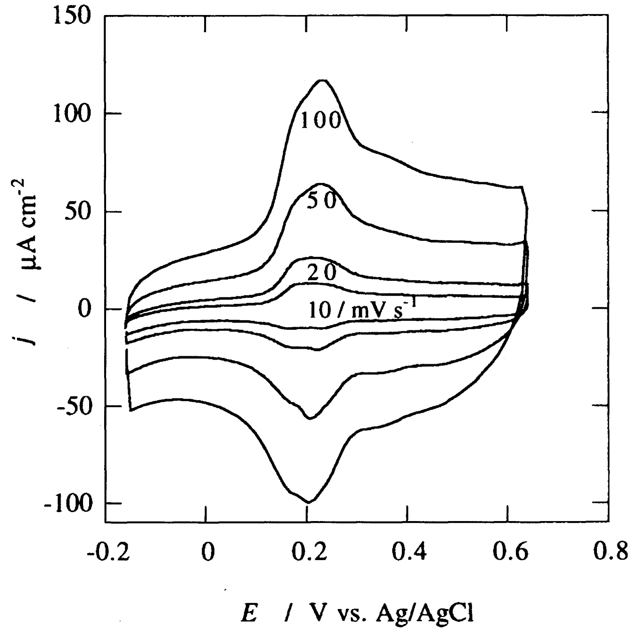

Fig. 4. Cyclic voltammograms using a roughened gold electrode measured in the same condition as Fig. 3.

Static SERS Spectroscopy. The chemical structures of the adsorbed species can be determined by static SERS spectra measured at a constant potential. Figure 5 shows SERS spectra measured at 0.40 and 0.05 V. The normal Raman spectrum of PQ in the solid state is also shown at the bottom in Fig. 5. Assignments of the characteristic frequencies of Raman lines were carried out based on the normal coordination analysis and experimental results reported previously for PQ[22] and phenanthrene.[23,24] The assignments are summarized in Table 1.

The frequencies of the SERS spectrum at 0.4 V are almost coincident with those of the normal Raman spectrum for neat PQ, except for slight shifts in the frequency. It can be said from the spectral coincidence between SERS and normal Raman spectra that the principal structure of PQ is preserved without any change of the chemical structure due to adsorption onto a gold electrode surface, although a decomposition of quinones was observed when Pt or Rh was used as an electrode.[25]

As for the adsorption of PQ on a gold electrode surface, C=O groups in the PQ molecule can be considered to con-

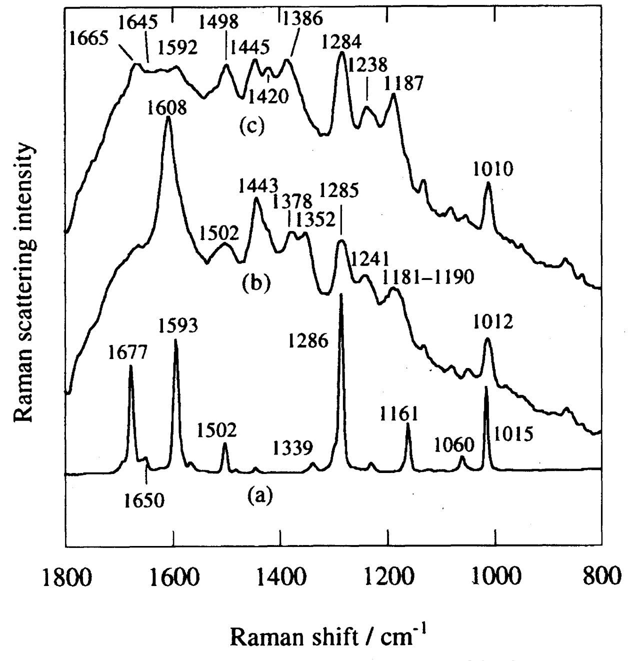

Fig. 5. Comparison between SERS spectra of 9,10-phenanthrenequinone (PQ) adsorbed on the gold electrode. (a) normal Raman spectrum of neat PQ, (b) PQ at 0.05 V, and (c) PQ at 0.40 V. Each spectrum was measured at 4 cm^{-1} resolution with 64 scans.

Table 1. Vibrational Assignment of Normal Raman Frequencies of PQ, SERS of PQ on Gold at 0.40 V vs. Ag/AgCl, and Its Reduced Form at 0.05 V

Observed frequency / cm^{-1}			
PQ (neat)	SERS of PQ (0.40 V)	SERS of reduced PQ (0.05 V)	Assignments[a)]
3070	2950—3070 (broad)	2940—3070 (broad)	C–H stretch
1677	1665		C=O sym. stretch
1650	1645		C=O asym. stretch
1593	1592	1608	C=C stretch
1502	1498	1502	C=C stretch
1445	1445	1443	C=C stretch
1418	1420	1422	C=C stretch
	1386	1378	—
		1352	C=C stretch+C–O bend
1339			—
1286	1284	1285	C=C stretch
1231	1238	1241	C=C stretch
1161	1187	1181-1190	C–H i.p. bend
	1132	1131	—
	1082	1080	—
1060	1054	1050	C–H i.p. bend
1015	1010	1012	C=C i.p. bend
781	766	766	C–H o.p. bend
466	467	464	C–H o.p. bend

a) i.p. = in-plane, o.p. = out-of-plane, sym. = symmetric, asym. = asymmetric. —: cannot be assigned.

tribute to the adsorption, since a large shift of 12 cm^{-1} to the lower wavenumber was observed for the C=O symmetrical stretching vibrational mode. If the π interaction is a major adsorptive motive force, the Raman line of ring deformation appearing at ca. 1000 cm^{-1} should be shifted largely toward a lower wavenumber. Such spectral shifts were reported for benzene derivatives.[26] The frequency of the ring deformation does not show a large shift, as shown in Fig. 5. From these results, it is suggested that there is a strong interaction between the oxygen atom of PQ and the electrode surface, and that the phenanthrene ring of PQ interacts weakly with a gold electrode. The broadness of the C=O Raman line around 1660 cm^{-1} at 0.4 V can be attributed to the diversity of the adsorption states.

As shown in Fig. 5(b), it can be easily recognized that Raman lines due to C=O stretching vibrational modes disappear and a new Raman line appears at 1352 cm^{-1}, which is assigned to a mixture of C=C stretching and neighboring C–O symmetric bending vibrational modes.[27] Based on the spectral changes shown in Fig. 5, chemical species on the gold electrode surface can be assigned to PQ and reduced PQ for the electrode potentials of 0.40 and 0.05 V, respectively. Thus, both redox species of PQ in Fig. 2 were confirmed to be present on the gold electrode. The PQ stability during the redox cycles was also confirmed from SERS spectra by repeated measurements.

Time-Resolved SERS Spectroscopy. In aprotic solvents, it is known that the reduction of quinones involves a two-step-one-electron reaction,[28] and the intermediate can be easily detected as a semiquinone radical by cyclic voltammetry. In contrast, a semiquinone radical is unstable and its lifetime is shorter in aqueous solutions than in aprotic solvents. However, Kano and Uno[16] proposed the presence of an intermediate to explain the nonideal behavior of cyclic voltammograms, such as broadening of peaks. Their proposal was based on a careful examination of cyclic voltammograms of PQ adsorbed on graphite electrodes using curve-fitting methods. They concluded that approximately 30% of the adsorbed species should change to the semiquinone radical form when the intermediate concentration has its maximum value during measurements of cyclic voltammograms. On the other hand, the existence of such intermediates has not been studied for gold electrodes. Accordingly, time-resolved SERS spectroscopy was applied to examine the intermediate in a redox reaction for a gold electrode.

Figure 6 shows a series of time-resolved SERS spectra of PQ adsorbed on a gold electrode. The spectra were measured at each time-slice of 1 ms, but is shown here with 5 ms intervals for simplification. The frequencies of the Raman lines in the time-resolved SERS spectra are slightly different from those in static SERS spectra, as shown in Figs. 5 and 6. In the static SERS, the chemical species are completely oxidized or reduced, although both oxidized and reduced species can coexist during stepping of the potentials. Initially, PQ was present as a reduced form and the spectrum was measured successively after the potential was stepped up from 0.05 to 0.40 V. After the potential was stepped up, the reduced PQ was oxidized to give PQ. In Fig. 6, the formation of PQ can

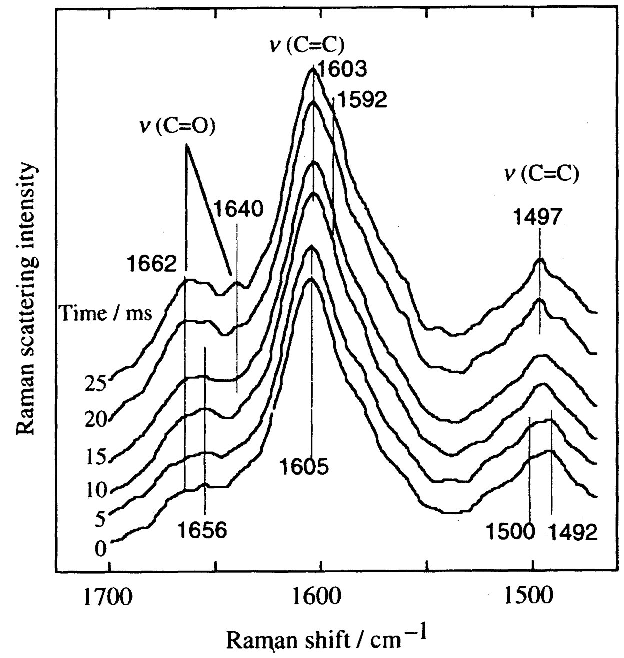

Fig. 6. Time-resolved SERS spectra of 9,10-phenanthrenequinone adsorbed on the gold electrode. Time 0 is when a potential was stepped up from 0.05 to 0.40 V vs. Ag/AgCl. Each spectrum was measured at 4 cm^{-1} resolution and its acquisition time was within 1 ms.

be confirmed based on the increasing Raman scattering intensities of both symmetric and asymmetric carbonyl stretching modes (1662 and 1640 cm^{-1}) after the potential step. A lower wavenumber shift of the C=C stretching vibrational mode around 1600 cm^{-1} indicates that the ring structure goes from a phenanthrene to a phenanthrenequinone. The spectral change was also measured for a reverse potential step (0.40 to 0.05 V), and a reversible spectral change was observed.

It can be recognized in Fig. 6, however, that the relative intensities of the Raman lines become remarkable in the time region from 15 ms to 25 ms. For example, the intensities of the C=O stretching vibrational modes appearing at 1656 and 1662 cm^{-1} gradually change with time. This intensity change cannot be attributed to radical formation,[25] because this would result in a much larger frequency shift. One possible explanation for this spectral change is that there would be some different adsorption states. First, reduced PQ adsorbs more strongly than does PQ via oxygen atoms. After oxidization by stepping up the potential to 0.4 V, PQ would suffer from a rearrangement and would take a form having a weaker interaction between the oxygen and the gold electrode surface than the reduced PQ. This explanation can be supported by the observation that the anodic current is larger than the cathodic one, as shown in Fig. 3. The larger anodic current reflects much desorption of the oxidized form from the gold electrode surface.

All Raman lines measured by time-resolved SERS can be assigned to either PQ or the two-electron-reduced form of PQ, and no new Raman lines which can be assigned to the intermediates of one-electron reaction products (semiquinone radical) were observed. It is possible that one-electron reacted intermediates may form on the electrode for a short period of time, but they rapidly transform to PQ within 0.5 ms after the potential step. Accordingly, the amount of the intermediates accumulated on the electrode surface is expected to be very low in the time region shown in Fig. 6.

Conclusion

The redox of 9,10-phenanthrenequinone on a gold electrode was examined by step-scan FT-SERS spectroscopy with a submillisecond time resolution; it was found that the amount of intermediate accumulated on the electrode surface was negligible in the ms time region. Although the time-resolution of step-scan time-resolved SERS spectroscopy is limited by the response time of the detector, the time resolution should be easily improved to the ns region if a faster detector, such as a near infrared photomultiplier tube, is used.

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