CHEMISTRY LETTERS, pp. 933-936, 1994.

Polymerization of Pyrrole on a Roughened Gold Electrode Studied by Surface Enhanced Raman Scattering

Wataru FUJITA, Toshio ISHIOKA,† Norio TERAMAE,*† and Hiroki HARAGUCHI
Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01
†Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980

The polymerization of pyrrole adsorbed on a roughened gold electrode was studied by surface enhanced Raman scattering (SERS) spectroscopy. It was found that pyrrole was polymerized at -0.2 V vs. SCE and under open circuit. It is concluded that the polymerization of pyrrole occurs by the catalytic action of adatoms on a roughened gold electrode because pyrrole is adsorbed with the molecular ring parallel to the surface plane.

Surface enhanced Raman scattering (SERS) spectroscopy is a well-known tool for the *in situ* study of trace amounts of organic molecules and their reaction products adsorbed on a metal surface.1) In our previous study, the reaction of thiophene adsorbed on a roughened gold electrode was investigated by use of SERS spectroscopy.2) It was found that thiophene oligomers and polythiophene were produced on the electrode surface at potential ranges of 0-0.6 V and 0.8-1.0 V vs. SCE , respectively.2) It is interesting to examine the reaction of pyrrole on metal surface, since the pyrrole molecule has a heterocyclic 5 membered ring which is similar to the structure of thiophene, and also forms conducting polymer by an electrochemical oxidation.3) In order to compare the reactivity of pyrrole with that of thiophene, in this study we have examined SERS spectra of pyrrole adsorbed on a roughened gold electrode.

All chemicals used in the present study were purchased from WAKO Chemical Co. Ltd. The solutions were prepared by using pure water and deoxygenated with argon gas before use.

The electrochemical cell used in the SERS experiment is consisted of three electrodes,4) *i.e.*, a working electrode of polycrystalline gold disk (φ 5 mm, Nilaco), a Pt counter electrode and a saturated calomel reference electrode (SCE). A gold working electrode was polished with 1 and 0.05 μm alumina slurries before use, and then it was roughened by keeping the electrode potential at 1.0 V vs. SCE for 10 min in 0.1 M KCl aqueous solution. After rinsing, it was set in the electrochemical cell containing an aqueous solution of 0.05 M pyrrole monomer and 0.1 M KCl. The SERS spectra were recorded with a Fourier Transform (FT) Raman spectrometer (Bomem RAMSPEC Model 151), where the excitation wavelength was 1064 nm of a Nd:YAG laser (Quantronix Model 114). The potential of the working electrode was controlled with a potentiostat (HOKUTODENKO Model HA-510) and a function generator (HOKUTODENKO Model HB-105).

Raman spectra of liquid pyrrole and polypyrrole film prepared by the conventional electrochemical method are shown in Fig.1. A typical SERS spectrum of pyrrole obtained at -0.2 V vs. SCE is also shown at the top of Fig. 1. The observed vibrational frequencies and their assignments are summarized in Table 1. Assignments are carried out according to the literatures.[5-7] It can be easily recognized that the spectrum presented in Fig.1c) is not essentially identical with the Raman spectrum of liquid pyrrole shown in Fig.1a), but that of polypyrrole shown in Fig.1b). This fact means that pyrrole on a roughened gold electrode is converted to conducting polymers during the SERS experiment. Since the polymerization of pyrrole takes place on a counter electrode at -0.3 V vs. SCE and lower potentials, further attempts were not carried out for obtaining SERS spectra of pyrrole at the potential range lower than -0.2 V vs. SCE. The potential of -0.2 V vs. SCE is significantly low compared to the potential used in the conventional electropolymerization of pyrrole monomer (0.8 V vs. Ag/AgCl in acetonitrile medium).

Martin et al.[8] and Bukowska et al.[9] reported that polymerization of pyrrole takes place during SERS experiments. Bukowska et al. observed the SERS spectra of pyrrole adsorbed on a roughened silver electrode, and suggested the polymerization of pyrrole. They concluded that the polymerization occurred on a roughened silver surface by a photochemical decomposition of AgCl induced by irradiation of Ar^+ laser.[9] However, in the present study, we use gold as an electrode and Nd: YAG laser (1064 nm) as an excitation source. Accordingly the polymerization does not occur by laser induced AgCl decomposition reaction. From the results shown in Fig.1, it is considered that the polymerization takes place on a roughened surface of gold electrode during SERS experiment. One can easily mention two possibilities about the origins of this polymerization. First, the polymerization might be promoted by Nd: YAG laser illumination. When an electrode is irradiated with a high intensity laser beam, several effects affect the electrode surface, such as photothermal effect,[10] photocurrent generation,[11] nonlinear effect,[12] and so on. One of these effects may be the cause of the polymerization of pyrrole. If the origin of this polymerization was laser illumination, the electrode potential at which polypyrrole was formed would depend on the intensity of an excitation source. The effect of laser illumination

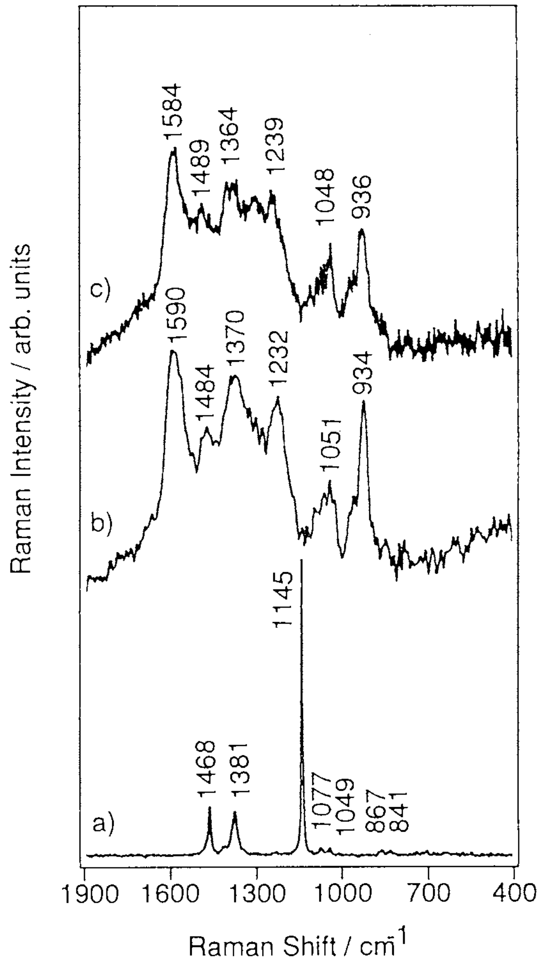

Fig. 1. Raman spectra of a) liquid pyrrole and b) polypyrrole film. c) SERS spectrum of pyrrole on a roughened gold electrode at -0.2 V vs. SCE.

Table 1. Raman frequencies and assignments of liquid pyrrole, polypyrrole and pyrrole on a roughened gold electrode

Frequencies / cm^{-1}			assignment5-7)
liquid pyrrole	polypyrrole film	SERS	
		-0.2 V vs. SCE	
	1590	1584	polaron and bipolaron ring stretching
1468	1484	1489	ring stretching
1381			
	1370	1364	bipolaron ring stretching
	1232	1239	bipolaron C-H in-plane-deformation
1145			ring stretching
1077			C-H in-plane-deformation
1049	1051	1048	
	934	936	polaron C-H in-plane-deformation
867			C-H out-of-plane-deformation
841			
711			ring out-of-plane-deformation

on the polymerization was examined by varing the laser power from 20 to 500 mW. All of the spectra obtained were very similar to the spectra shown in Figs. 1b) and 1c). This fact means that the polymerization is not caused by laser illumination. Second, the polymerization might be promoted by adatoms. When a surface of a gold electrode is roughened, it is known that adatoms are formed on the surface, and that adatoms have a strong activity of catalysis.13) In fact, there have been several reports on the catalytic reaction by adatoms during SERS observations.14,15) From our SERS experiments, it was found that the polymerization took place even under open circuit. Thus, it can be said that the polymerization is not due to the electrode process but the chemical process. On the other hand, thiophene did not polymerize under open circuit.2) If the origin of polymerization of thiophene on a roughened gold electrode was due to adatoms on an electrode surface, the polymerization would take place at a lower potential than 0.8 V vs. SCE. Therefore, the polymerization of thiophene takes place through the electrode process.

The polymerization mechanism discussed above is interpreted from the viewpoint of molecular orientations on the metal surface. It is reported that the orientation of thiophene on metal surface is differenet from the case of pyrrole. From the HREELS studies16,17) it is indicated that a pyrrole molecule is adsorbed on the metal surface *via* π electrons, with pyrrole ring parallel to the electrode surface. In the flat-on geometry on the surface, the π electrons of pyrrole ring can easily interact with adatoms on metal surface. However, thiophene is adsorbed with a vertical orientation in which the rings are perpendicular to the surface,16,17) and no polymerization takes place under open circuit. The polymerization of molecules adsorbed on a roughened gold surface occurs only when the molecules can easily interact with the surface adatom. Therefore, it can be said that pyrrole was polymerized by adatoms at -0.2 V vs. SCE and under open circuit, in contrast to the case of thiophene.

It is concluded that the origin of polymerization of pyrrole investigated in this study is different from that of thiophene, and that the origin is the catalytic action of adatoms on a roughened gold electrode. Further study on the catalytic reaction between pyrrole and adatom on a roughened gold electrode is now in progress.

References

1) "Surface Enhanced Raman Scattering," ed by R. K. Chang and T. E. Furtak, Plenum, New York(1982).
2) W. Fujita, N. Teramae, and H. Haraguchi, *Chem. Lett.*, **1994**, 511.
3) A. F. Diaz, K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, **1979**, 635.
4) J.-Y. Jin, N. Teramae, and H. Haraguchi, *Chem. Lett.*, **1993**, 101.
5) Y. Furukawa, S. Tazawa, Y. Fujii, and I. Harada, *Synth. Met.*, **24**, 329(1988).
6) B. Tian and G. Zerbi, *J. Chem. Phys.*, **92**, 3886(1990).
7) "Characteristic Raman Frequencies of Organic Compounds," ed by F. R. Dollish, W. G. Fateley, and F. F. Bentley, John Wiley & Sons, New York(1974).
8) F. Martin A. C. Prieto, J. A. de Saja, and R. Aroca, *J. Mol. Spectrosc.*, **174**, 363(1988).
9) J. Bukowska and K. Jackowska, *Synth. Met.*, **35**, 135(1990).
10) J. L. Valdes and B. Miller, *J. Phys. Chem.*, **93**, 7275(1989).
11) D. S. Corrigan and M. J. Weaver, *J. Electroanal. Chem.*, **228**, 265(1987).
12) Y. R. Shen, *Nature*, **337**, 519(1989).
13) M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **60**, 259(1975).
14) F. J. Boerio, W. H. Tsai, P. P. Hong, and G. Montaudo, *Macromolecules*, **22**, 3955(1989).
15) P. G. Roth, R. S. Venkatachalam, and F. J. Boerio, *J. Chem. Phys.*, **85**, 1150(1986).
16) B. A. Sexton, *Surf. Sci.*, **163**, 99(1985).
17) J. Y. Gui, D. A. Stern, F. Lu, and A. T. Hubbard, *J. Electroanal. Chem.*, **305**, 37(1991).

(Received February 23, 1994)