CHEMISTRY LETTERS, pp. 511-514, 1994.

Formation of Thiophene Oligomers and Polythiophene on a Roughened Gold Electrode Studied by Surface Enhanced Raman Scattering

Wataru FUJITA, 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

Thiophene adsorbed on a roughened gold electrode was studied in an aqueous solution at various potentials from 0 to 1.0 V vs. SCE by use of surface enhanced Raman scattering. 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, respectively. This potential range is significantly low compared to the potential used in the conventional electropolymerization of thiophene monomer (1.6 V vs. Ag/AgCl) in acetonitrile medium).

Electropolymerization is a convenient method for the synthesis of conductive polymer films such as polypyrrole,[1)] polyaniline,[2)] and polythiophene.[3)] This method is applicable to the preparation of electronic devices such as electrochromic displays, rechargeable batteries, transistors, and capacitors. As for polythiophene, it is known that thiophene is easily electropolymerized in acetonitrile solution to yield a film with high conductivity. In order to characterize the conducting polymer films, it is important to investigate about the adsorption behaviors of organic monomers on the electrode surface. Surface enhanced Raman spectroscopy (SERS) offers the possibilities for the *in situ* study of trace amounts of adsorbed organic monomers and their reaction products.[4)] Hence, in the present work, we have examined SERS spectra of thiophene adsorbed on a roughened gold electrode. It was found that adsorbed thiophene is oxidized at a relatively low electrode potential, to produce oligomers and polymers.

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 was almost similar to that one reported in a literature,[5)] consisting of three electrodes, *i.e.*, a working electrode of polycrystalline gold plate (10 × 10 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 performing sequential oxidation-reduction cycles (ORCs) in 0.1 M KCl aqueous solution. After rinsing, it was set in the electrochemical cell containing an aqueous solution of 0.03 M thiophene monomer and 0.1 M KCl. The potential of the working electrode was controlled with a potentiostat (YANACO Model VMA-010). 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 (Quatronix Model 114) operating at 500 mW.

Typical SERS spectra of thiophene obtained at several different electrode potentials are shown in Fig. 1, and the vibrational frequencies and assignments are summarized in Table 1. In this table, Raman shifts of liquid thiophene are also listed as a reference. From the SERS spectra shown in Fig. 1, it can be easily recognized that some bands newly appeare compared with a spectrum of neat thiophene. The Raman bands near 1150~ 1230 cm^{-1} arise mainly from the inter-ring C-C stretching mode in the oligomers.6) The band at 1283 cm^{-1}, one of the two bands appeared newly in Fig.1 a-c), is the C-H in-plane bending mode which was also observed in the infrared spectra of vapor thiophene7) and has become Raman active in the surface adsorbed state. The band at ca. 1520 cm^{-1} observed in Fig. 1 a-d) was assigned to the effective conjugation-coordinate mode which is associated with C-C and C=C skeletal bonds involved in a delocalisation path.8) This band is characteristic of thiophene oligomers. As a number of thiophene rings increased, the monotonical frequency shifts of this mode was observed in the Raman spectra in solution,8) that is, bithiophene (2T) 1556 cm^{-1}, terthiophene (3T) 1530 cm^{-1}, quaterthiophene (4T) 1519 cm^{-1}, and sexithiophene (6T) 1507 cm^{-1}. In other words, the Raman shifts decrease as the conjugation length increases. The Raman shift of the effective conjugation-coordinate mode gives information about the polymerization degree of oligomers in solution. Sarkar et al. reported SERS spectra of 2T,9) 3T,10) 4T,9) and 6T11) adsorbed on a silver colloid surface in acetonitrile. The effective conjugation coordinate modes of these molecules were observed at 1509 cm^{-1}(2T), 1508 cm^{-1}(3T), 1506 cm^{-1} (4T) and 1507 cm^{-1}(6T). These frequencies of oligothiophenes adsorbed on a colloidal silver decrease considerably compared with that of free oligothiophenes. The red-shift of the effective conjugation coordinate mode indicates an increase of conjugation length of the molecules adsorbed on a metal surface. Oligothiophenes in solution are anticoplaner, and so the molecules are anti but twisted. This suggests that the twist angle of thiophene decrease and the molecules become coplanar when oligomers are adsorbed on the surface of silver colloid. In the present work, it can be shown the structure of thiophene oligomers adsorbed on a gold electrode is similar to that in solution.

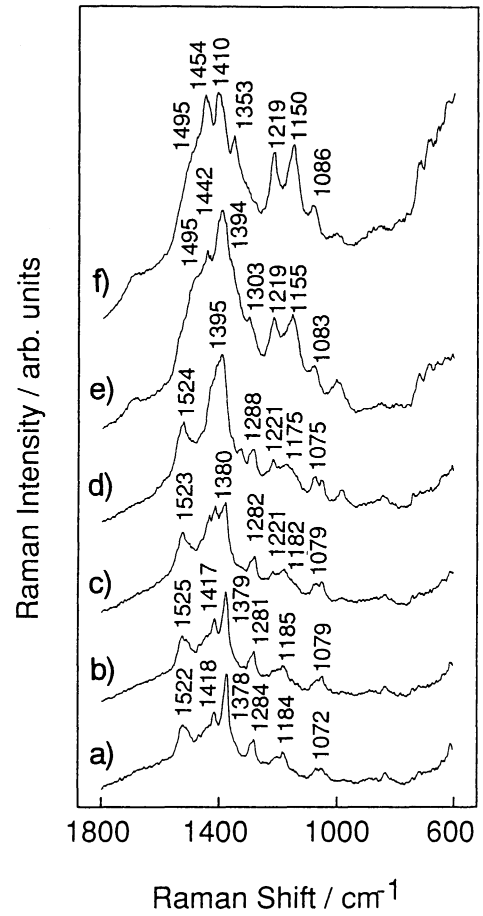

Fig. 1. SERS spectra of 0.03 M thiophene on a roughened gold electrode in 0.1 M KCl aqueous solution. The electrode potential was initially set at a) 0 V, and then increased to b) 0.2 V, c) 0.4 V, d) 0.6 V, e) 0.8 V and f) 1.0 V vs. SCE.

In order to identify the spectra shown in Fig. 1e) and 1f), these spectra were compared with a Raman spectrum of doped polythiophene film prepared on a Pt electrode from a dried Et_4NClO_4 (0.1 M) and thiophene

Table 1. Vibrational frequencies and assignments of Raman spectrum of liquid thiophene and SERS spectra of thiophene on a roughened gold electrode at various potentials

Liquid thiophene	Electrode potential (V vs. SCE)						Assignment[6-8]
	0	0.2	0.4	0.6	0.8	1.0	
	1522	1525	1523	1524			effective conjugation coordinate mode
	1471		1433		1442	1454	C=C symmetric stretching
1408	1418	1417	1410			1410	
1364	1378	1379	1380	1395	1394		
				1329	1303	1353	
	1284	1281	1282	1288			C-H in-plan bending (infrared active)
		1220	1221	1221	1219	1219	C-C inter-ring stretching
	1184	1185	1182	1175	1155	1150	
1086	1072		1079	1075	1083	1086	C-H in-plan bending
1038	1054	1052	1052	1055			

(0.1 M) in acetonitrile solution applying a potential at +1.60 V (vs. Ag/AgCl) for four minutes according to the usual electrochemical polymerization.[3)] The Raman spectrum of polythiophene film is shown in Fig.2b). The spectra in Fig.1e) and 1f) were almost similar to the Raman spectrum of polythiophene film. The shoulder near 1495 cm^{-1} is assigned to the effective conjugation-coordinate mode of polythiophene because this band intensity of polymer is considered to be very weak. The band near 1450 cm^{-1} arises from a symmetric C=C intraring stretching mode which is also characteristic of polythiophene. These results suggest that polythiophene was formed on the electrode surface at the potential range between 0.8 and 1.0 V. This potential range is significantly low compared to the potential for the usual electropolymerization of thiophene monomer. The electropolymerization has been usually achieved at 1.6 V (vs. Ag/AgCl) in acetonitrile solution. At the potential range from 0 to 0.6 V, thiophene oligomers are formed since the spectra shown in Fig. 1a-d) are different from the spectra of polymers and monomers.

Bukowska et al. observed the SERS spectra of thiophene molecules adsorbed on a roughened silver electrode, and suggested the oligomerization of thiophene molecules. They concluded that the oligomerization of thiophene molecules on a roughened silver surface occurred by a photochemical decomposition of AgCl induced by irradiation of Ar$^+$ laser.[12)] However, in the

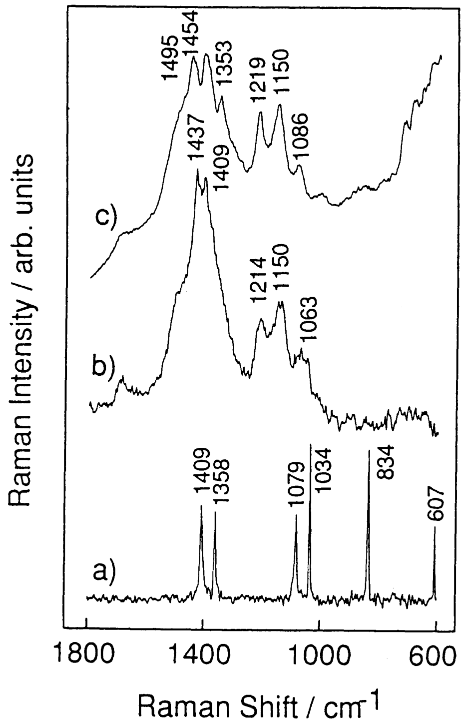

Fig. 2. Raman spectra of a) liquid thiophene and b) polythiophene. c) SERS spectrum of thiophene adsorbed on a roughened gold electrode at 1.0 V vs. SCE.

present sudy, we use a gold as an electrode and YAG laser (1064 nm) as an excitation source. Accordingly, the polymerization of thiophene molecules on a roughened gold electrode does not occur by laser induced-photochemical reaction. Further study on the reaction mechanism is now in progress.

References

1) A. F. Diaz, K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, **1979**, 635.
2) J.-Y. Jin, N. Teramae, and H. Haraguchi, *Chem. Lett.*, **1993**, 101.
3) G. Tourllon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173(1982).
4) R. K. Chang and R. K. Furtak, "Surface Enhanced Raman Scattering," Plenum, New York (1982).
5) P. Gao, M. L. Patterson, M. A. Tadayyoni, and M. J. Weaver, *Langmuir*, **1**, 173(1985).
6) Y. Furukawa, M. Akimoto, and I. Harada, *Synth. Met.*, **18**, 151(1987).
7) F. R. Dollish, W. G. Fateley, and F. F. Bentley, "Characteristic Raman Frequencies of Organic Compounds," John Wiley & Sons, New York(1974).
8) G. Zerbi, B. Chierichetti, and O. Inganas, *J. Chem. Phys.*, **94**, 4637(1991).
9) U. K. Sarkar, S. Chakrabarti, A. J. Pal, and T. N. Misra, *Spectrochim. Acta*., **48A**, 1625(1992).
10) U. K. Sarkar, S. Chakrabarti, and T. N. Misra, *Chem. Phys. Lett.*, **190**, 59(1992).
11) U. K. Sarkar, S. Chakrabarti, T. N. Misra, and A. J. Pal, *Chem. Phys. Lett.*, **200**, 55(1992).
12) J. Bukowska and K. Jackowska, *Synth. Met.*, **35**, 135(1990).

(Received November 22, 1993)