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Change of Raman Scattering Intensity of a Polypyrrole Film during Reversible Doping and Emitting Processes of ClO_4^-

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Symmetric and antisymmetric streching modes were observed in an *in situ* Raman scattering response of a polypyrrole(PPY) film electrode in the course of a redox doping and emitting of a ClO_4^- anion. Anion doping arose a deformation of PPY conformation due to a complex formation between ClO_4^- and a positive hole.

One dimensional polymers such as polypyrrole, polythiophene, and polyacethylene synthesized by the chemical or electrochemical technique have attention as the organic conductors because of their electric and electronic properties. These thin films have been recently designed for applications to a high electric conductor, a semiconductor device, an electrochromic device, and a thin film battery.[1-3)]

Polypyrrole(PPY) is one of the stable conductive organic polymers. Emphasis on the properties of the polymer is derived from the behaviour of redox doping-emitting processes, i.e., doping of charged ions to PPY and emitting of doped ions from PPY. Therefore, the investigation on an electric conductivity and electronic spectra for doped and emitted polymers, as well as theoretical approaches, have been carried out.[4,5)] With respect to a polymer conformation, although studies on vibrational spectra have been reported for $(CH)_x$, there are few for PPY.[6,7)]

In this study, the *in situ* Raman scattering spectra were monitored in order to obtain information on a PPY film in the course of a redox process and the effect of anion doping on a polymer conformation is discussed.

PPY film was prepared on an indium tin oxide (ITO) electrode by oxidation of pyrrole in an acetonitrile solution with 0.1 mol dm^{-3}(=M) tetrabutyl ammonium perchlorate (TBAP) at the potential of 1.2 V *vs*. an Ag reference electrode, as described in elsewhere.[8)] Film thickness was controlled by the oxidation charge, where thickness of 1500 Å was obtained by polymerization of 60 mC. Redox property of a PPY film accompanying doping and emitting of a ClO_4^- anion was measured by the electrochemical measuring system using a potentiostat (Nikkou Keisoku Co.). Absorption spectra were measured by an *in situ* method in the course of redox electrolysis of a polypyrrole film. *In situ* Raman scattering spectra were also measured in a spectro-electrochemical system with a Nihon Densi Raman scattering spectrometer, as shown in Fig. 1.

Absorption spectra of PPY in a redox cycling between doping and emitting of a perchlorate anion are shown in Fig. 2. The spectra of doped and emitted PPY are clearly different. Anion-doped PPY film has an absorption peak at the wavelength of 1200 nm ($\varepsilon = 4.5\mathrm{x}10^{4}$), on the contrary the anion-emitted PPY film has a peak at 400 nm ($\varepsilon = 4.6\mathrm{x}10^{4}$) when the film is reduced. The absorption spectra are based on the electronic charge distribution of the PPY film. The peak of emitted PPY is ascribed to the absorption of π-π^* transition of a conjugated bond in PPY. Another peak of doped PPY is ascribed to a plasmon absorption, derived from a complex formation between a positively charged pyrrole and an anion in the one-dimensional PPY chain. These two types absorption have resulted from the redox of PPY. Similar phenomenon in the spectra change due to anion doping has been reported for $(CH)_x$.

It is presumed that the vibration of the charge distribution of a PPY film due to the anion doping and emitting processes can affect the bond structure of PPY chain, as well as the absorption spectra. In order to investigate the redox effect on the polymer conformation, the Raman scattering spectra of a PPY film electrode surface were observed in an in situ condition in the course of a redox electrolysis of PPY. Figure 3 shows the Raman scattering spectra of anion-doped and emitted PPY films. The observed spectrum of a doped PPY film can be clearly distinguished from that of an emitted film. Clear difference between doped and emitted PPY films appears at the wave numbers from 800 to 1800 cm^{-1}. The spectral peaks appeared in doped PPY are 1100, 1170, 1250, 1420, 1610 cm^{-1}, while those in emitted PPY are 1080, 1170, 1250, 1280, 1450 cm^{-1}.

These Raman scattering peaks are assigned from the data of pyrrole derivatives,9) which are listed in Table 1. Taking account of the vibrational mode of a PPY linkage, symmetrical modes (A) are major in emitted PPY, on the contrary antisymmetrical modes (B) are major in doped PPY. Therefore, doping treatment can have a clear effect on the PPY conformation.

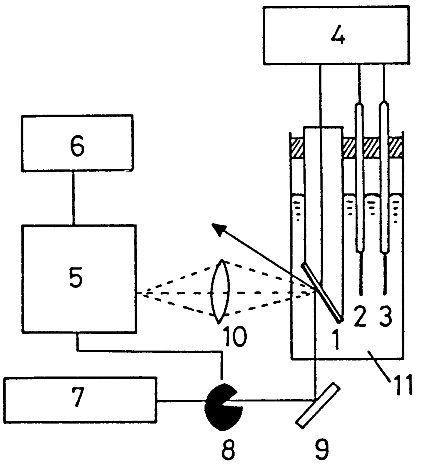

Fig.1. Experimental system.
1; PPY, 2; Pt, 3; Ag, 4; potentiostat, 5; monochromator, 6; lock-in amplifier, 7; Ar ion laser, 8; light chopper, 9; mirror, 10; lens, 11; electrolytes.

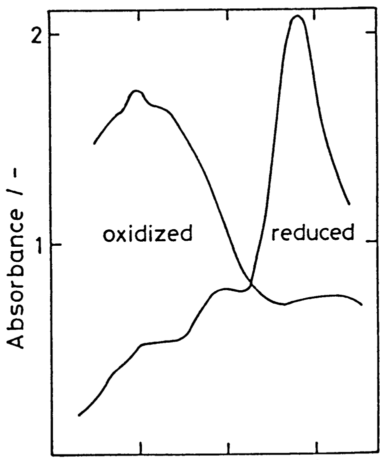

Fig. 2. Absorption spectra of oxidized and reduced PPY film electrodes.

Table 1. Characteristic frequencies in the Raman spectra of pyrrole derivatives

Bond	Mode	Frequency / cm^{-1}			
		Pyrrole	2-Substituted Pyrrole	2,5-Substituted Pyrrole	PPY film electrode[a)]
NH	A	3495	3385-3380		3500-3400
CH	B	3133-3100	3120-3045		3300-3200
C=C(Ring)	B	1530	1570-1560	1605	1610-1600 (Ox)
C=C(Ring)	A	1467	1475-1460	1514	1450 (Red)
C-N(Ring)	B	1418	1420-1400	1418	1420 (Ox)
C-N(Ring)	A	1379			1380 (Red)
CH	A	1237		1258	1250
Ring Breathing	A	1114			1170

a) Ox and Red denote the characteristic responses of oxidized and reduced PPY electrodes, respectively.

Figure 4 shows the response of Raman scattering intensity at 1620 cm^{-1}, which is due to an antisymmetric C=C bond streching mode, when the potential was applied stepwise to a PPY film electrode. The response of the scattering signal increases by an oxidative doping and decreases by a reductive emitting of a doped anion with an increase of electric charges, and shows a reversibility against the redox control. This fact means that the PPY conformation changes due to a charge transfer of PPY.

From an electrochemical redox reaction of PPY, the charge transfer process accompanying with anion doping and emitting is described as,

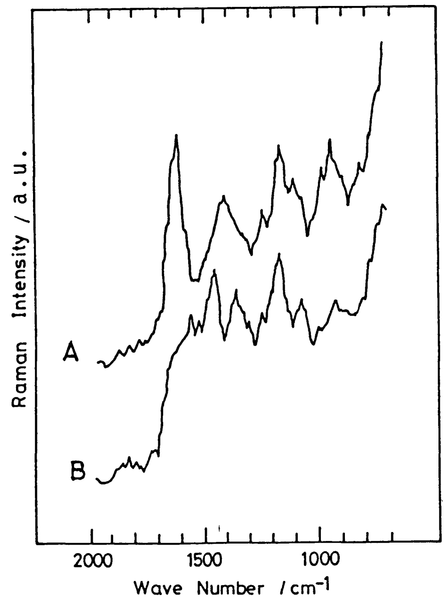

Fig. 3. Raman scattering spectra of doped (A) and emitted (B) PPY film electrodes.

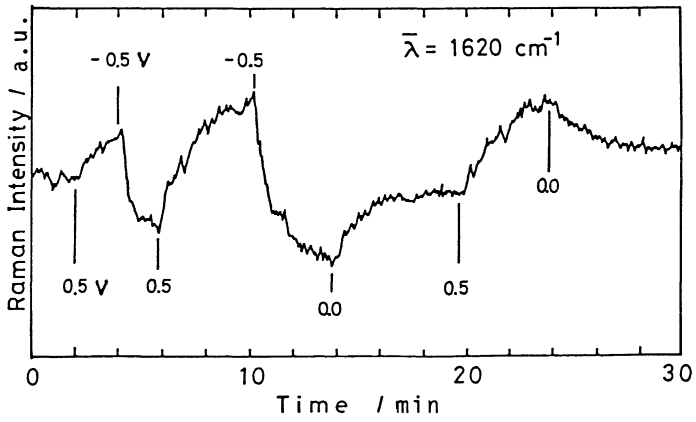

Fig. 4. Potential dependence of Raman scattering intensity at 1620 cm^{-1} for a PPY film electrode. Doping at 0.5 V, Emitting at -0.5 V.

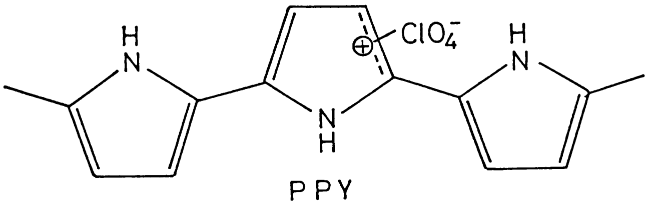

Fig. 5.
Schematic illustration for a PPY conformation doped with a ClO_4^- anion.

$$PPY + ClO_4^- - e^- \rightleftharpoons PPY^+\text{-}ClO_4^- \qquad (1)$$

where a positive sign on PPY^+ denotes a positive hole which resulted from an anion doping. An electrical neutrality within PPY is guaranteed by a formation of a PPY^+-ClO_4^- complex. A pair formation between a positive hole and a ClO_4^- anion affects the charge distribution due to lack of π electrons on PPY, and gives rise to a deformation in a polymer linkage. From an appearance of an anti-symmetric mode in the Raman scattering spectra of doped polypyrrole, it is thought that a positive charge is restrined at a certain C=C bond of PPY, and not at delocalized π electrons spreaded over a pyrrole ring, then forming a complex with ClO_4^-, as schematically illustrated in Fig. 5.

The charged complex has been treated as a charged soliton or a bipolaron which behaves as a collective motion in the electric and electronic properties.[10,11] Although more quantitative relationship between Raman response and physical properties of PPY would be needed for detailed interpretation, we conclude here that the Raman scattering response reflects an effect of a charged complex upon a PPY conformation.

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