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Characteristics of the ring stretching of oxidized polypyrrole on the surface-enhanced Raman spectrum

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Abstract In this study, polypyrrole (PPy) films were electropolymerized under different preparation conditions on rough gold substrates. The peak shown at the higher frequency of the double peaks at about 1329 and 1386 cm^{-1} in surface-enhanced Raman scattering of PPy was initially assigned to the ring stretching of oxidized PPy. A systematic study was carried out to confirm this assignment. It was found that the conductivity of PPy was strongly related to and increased with this Raman peak intensity of oxidized PPy. Meanwhile, the normalized relative intensities of this Raman peak for various PPy films are consistent with their corresponding doping levels.

Keywords Oxidized polypyrrole · Conductivity · Surface-enhanced Raman scattering

Introduction

In recent years, polypyrrole (PPy) films have been extensively studied in microelectronic devices, batteries and gas sensors [1, 2, 3, 4]. Generally, films synthesized by electrochemical polymerization have the advantages of exhibiting higher conductivity and stability to air [5, 6, 7]. Furthermore, many factors can influence the physical and spectroscopic properties of PPy [8, 9, 10, 11, 12], including the nature of the solvents and supporting electrolytes employed in the preparation, whether it is in the oxidized or reduced state, the pH in solution, as well as the monomer and electrolyte concentrations. Also, the procedure of treating PPy with

water after its preparation to remove monomers and supporting electrolytes can change its properties. Therefore, many methods [13, 14, 15, 16] have been employed to measure the properties of PPy in various states. Generally, the conductivity of doped PPy is primarily dependent on the doping level and the kinds of dopants [17, 18]. From XPS experiments [19, 20] it was seen that the doping level changed with the treated PPy according to the level of acidity; as a result, the corresponding conductivity also changed.

Raman spectroscopy [21, 22, 23, 24] is an invaluable method to evaluate the structural situation of PPy in various states. Nevertheless, the information provided can be reduced owing to weak signals or interference from noise [21, 22]. In general, the Raman technique cannot be applied to the analysis of organic compounds that are present at very low levels in a system. However, there are two useful exceptions to this rule [25]. Two methods for increasing the signal of a species presenting very low levels are resonance-enhanced Raman spectroscopy (RRS) and surface-enhanced Raman scattering (SERS). One of the major considerations for the formation of a SERS surface is surface roughness, which has been achieved in various ways [26, 27]. As shown in the literature [26, 28, 29], a broader Raman peak of PPy appears in the range 1300–1410 cm^{-1} , which is assigned to ring stretching. However, distinguishable double peaks at about 1331 and 1385 cm^{-1} can be seen in this range, as shown in previous research [30], but further studies to identify these double peaks have been less reported in the literature. Some efforts have been made to correlate the conductivities of PPy films in various states with their corresponding Raman peaks of the backbone stretching of C=C bonds [24, 31] and doping levels obtained from XPS analysis [19, 20]. Nevertheless, the correlation has not yet been made between the conductivity of PPy and the relative intensities of Raman peaks for the ring stretching of PPy.

This work proposes a relationship between the intensity of the Raman peak for the ring stretching of oxidized PPy and its corresponding conductivity. Four

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pairs of different PPy films were prepared on roughened gold substrates, accompanied with conductivity measurements, to identify the peak for the ring stretching of oxidized PPy on the SERS spectra.

Experimental

In SERS experiments, before the electropolymerization of PPy, Au electrodes were roughened by oxidation-reduction cycles (ORC) in a separate cell, as reported elsewhere [30]. Then, the electrochemical synthesis of different PPy films was carried out on the roughened Au substrates. Two kinds of oxidized PPy films were prepared in aqueous solution (sample 1) and in acetonitrile solution (sample 2), deoxygenated with nitrogen and containing 0.1 M pyrrole and 0.1 M LiClO₄, at constant onset oxidation potentials of 0.8 V vs. Ag/AgCl and 0.9 V vs. SCE, respectively. The treated PPy film (sample 3) was prepared by treating the oxidized PPy, prepared in aqueous solution, with water for 0.5 h. The fully reduced PPy film (sample 4) was prepared by reducing the oxidized PPy, prepared in aqueous solution, in an aqueous solution containing 0.1 M LiClO₄ at a constant cathodic potential of -0.4 V vs. Ag/AgCl until the current approached zero. Over-oxidized PPy film (sample 5) was prepared as prepared in sample 1 but an anodic potential of 1.2 V vs. Ag/AgCl was used instead of 0.8 V vs. Ag/AgCl. All electrochemical experiments were performed in a three-compartment cell controlled by a potentiostat (model PGSTAT20, Eco Chemie), and were maintained at room temperature (25 °C).

Before the conductivity measurements, prepared PPy films were stripped from the electrodes with Scotch Tape and had a mechanical stability that made them well suited for the measurements. Then the conductivities were determined using a commercial instrument (model RT-7, Napson), applying the four-probe technique with a direct current at 25% relative humidity and 25 °C. Raman spectra were obtained using a Renishaw 2000 Raman spectrometer employing a He-Ne laser of 25 mW and a charge couple device (CCD) detector with 1 cm⁻¹ resolution.

Results and discussion

Inspecting the conductivities of various PPy films shown in Table 1 reveals that PPy prepared in acetonitrile solutions has the advantage of a higher conductivity than that prepared in aqueous solutions. It also indicates that PPy loses its conductivity after being treated with water for 0.5 h. Meanwhile, the conductivity performance of various PPy films, except for sample 5 of over-oxidized PPy, is consistent with the results of their

corresponding N⁺/N ratios, which is generally equal to the doping levels [32], as exhibited in Table 1. Namely, over-oxidized PPy with a higher conductivity is always accompanied with a higher doping level. Generally, a higher polymerization potential gives the advantage of a higher oxidation level, contributing to a high level of conductivity. As reported in a previous study [33], a higher doping level of 0.37 for sample 5, but corresponding to a markedly lower conductivity of 9.5 S cm⁻¹, reveals that over-oxidation [34] and side reactions compete with the film-forming reaction [17] during polymerization of PPy at 1.2 V vs. Ag/AgCl, resulting in some extent of ring opening and pyrolysis. In previous studies [24, 31], the correlation between the conductivities of PPy films in various states with their corresponding Raman peak positions for the backbone stretching of C=C bonds had been established. However, no further discussion had been done, such as the correlation between the conductivity and the double peak intensities of the ring stretching of PPy, or the assignment of the peaks.

Figure 1 shows the SERS spectra of various PPy films. Comparing the Raman double peaks for ring stretching in the range of 1300–1450 cm⁻¹ in the spectra (a) and (b), it can be seen that the relative intensity of the peak at the higher frequency is significantly larger for PPy polymerized in acetonitrile solutions than for PPy polymerized in aqueous solutions. The treatment effect of the oxidized PPy with water for 0.5 h can be examined by comparing the spectra (a) and (c). The aim of this treatment is to remove the monomer and other soluble molecules. However, the properties of PPy may change and the conductivity decay may also occur due to this treatment [20]. The peak at about 932.0 cm⁻¹ in the figure is assigned to the symmetric stretching mode of ClO₄⁻ dopants [23]. The main peak is always accompanied with a broad shoulder on the high frequency side, which is assigned to the incorporated salts [23]. After treatment with water, the magnitude of this shoulder reduces. This indicates that the water treatment indeed exhibits the function of removing supporting electrolytes, not doped anions, from the PPy matrix. However, it is important to distinguish the

Table 1 Performance of various PPy films on the conductivity, doping level, and Raman peaks of various scattering modes

Sample ^a	Conductivity (S cm ⁻¹)	N ⁺ /N ratio [32]	Raman peak position for ring stretching (cm ⁻¹)			Raman peak position for C=C bond stretching (cm ⁻¹)
			Low frequency	High frequency	Normalized relative intensity ^b	
1	25.9	0.25	1328.8	1386.2	3.02	1601.5
2	110	0.32	1332.6	1376.7	8.72	1591.1
3	10.5	0.20	1332.6	1376.4	0.314	1608.8
4	0.012	0.052	1326.3	1411.5	0.296	1614.4
5	9.5	0.37	1332.1	1384.7	3.06	1609.7

^adescribed in experimental

^bcalculated from the ratio of the relative intensity of the peak at the high frequency to that of the peak at the low frequency. The relative intensity is the intensities difference between the peak and the background defined as the valley between the double peaks of ring stretching

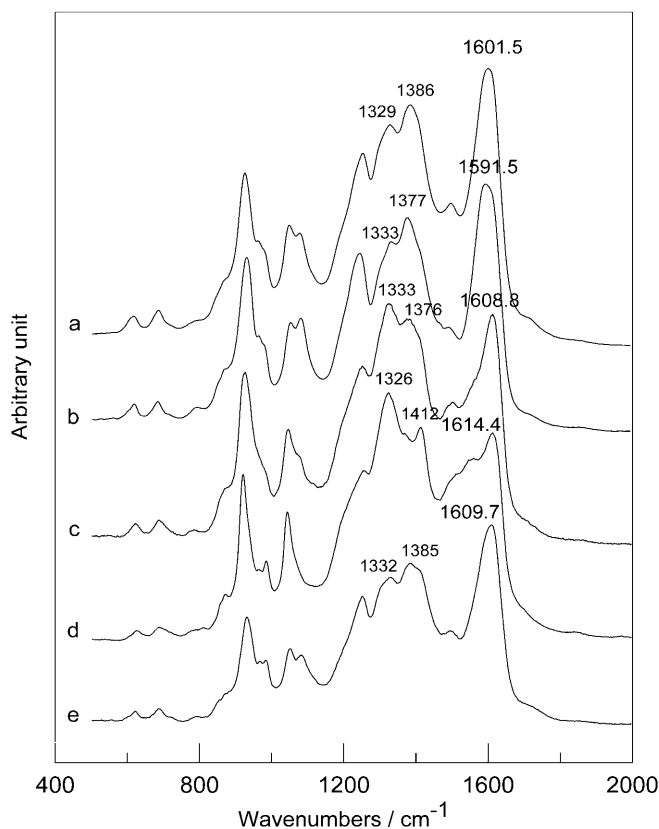


Fig. 1 SERS spectra of various PPy films. (a) Oxidized PPy prepared in aqueous solution (sample 1). (b) Oxidized PPy prepared in acetonitrile solution (sample 2). (c) Water-treated PPy (sample 3). (d) Fully reduced PPy (sample 4). (e) Over-oxidized PPy (sample 5)

spectral differences in the range 1300–1450 cm^{-1} . In this range for ring stretching, the peak located at the higher frequency side of the double peaks becomes insignificant after treating with water for 0.5 h. This decrease in conductivity clearly indicates that this treatment partially reduces the purely oxidized PPy. Meanwhile, the Raman peak for the stretching of C=C bonds shifts from 1601.5 to 1608.8 cm^{-1} after treatment with water.

The influence of completely reducing the oxidized PPy on the Raman peaks can be found from comparing spectra (a) and (d) in Fig. 1. These phenomena are similar to that discussed above in the spectral differences after treating oxidized PPy with water. From the conductivity measurements, it can be seen that the originally oxidized PPy reduces to its neutral state and loses its conductivity during reduction. Also, the effect of PPy films polymerized at an over-oxidation potential of 1.2 V vs. Ag/AgCl on the Raman peaks can be inspected from comparing spectra (a) and (e). Except for the fact that the C=C backbone stretching shifts from 1601.5 to 1609.7 cm^{-1} owing to the corresponding lower conductivity resulting from over-oxidation of PPy, the other Raman peaks are similar.

The performances of the Raman peaks of various PPy films, together with their corresponding conduc-

tivities, are listed in Table 1. As demonstrated in this table, if PPy films have lower conductivities, the peak for C=C bond stretching shifts toward a higher frequency. However, it is difficult to quantitatively correlate these shifts with the changes in conductivity. Nevertheless, it can be found that the conductivity of PPy, except for over-oxidized PPy, increases with the increase of the normalized relative intensity of ring stretching. This reveals that the normalized relative intensity is more meaningful for evaluating the conductivity change of PPy. Therefore, the peak shown at the higher frequency side in the spectrum range 1300–1450 cm^{-1} can be assigned to the ring stretching of oxidized PPy. This can be considered as an indication of the conductivity of PPy.

Conclusion

From the results discussed above, the peak shown at the higher frequency side of the double peaks at about 1329 and 1386 cm^{-1} can be undoubtedly assigned to the ring stretching of oxidized PPy. Four pairs of different PPy films (oxidized and fully reduced, oxidized and over-oxidized, with and without treated with water, and prepared in water and in acetonitrile) were prepared to successfully confirm this assignment. The conductivity of PPy is strongly related to and increases with this peak intensity of oxidized PPy, like the performance of the peak position of C=C bonds on the conductivity of PPy. Meanwhile, the normalized relative intensities of this Raman peak for various PPy films are consistent with their corresponding doping levels.

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