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Preliminary Investigation of Iron Protoporphyrin SAMs on Platinum Electrodes by Surface Enhanced Vibrational Spectroscopies

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Abstract: *In situ* SERS and ATR-SEIRAS were applied to investigate the electrochemical and structural properties of iron protoporphyrin IX (FePP) self-assembled monolayers (SAMs) on Pt electrodes in 0.1 mol·L^{-1} $HClO_4$. The potential dependent SERS spectra of the FePP SAM on a roughened Pt electrode with the enhancement factor of ca. 40 were acquired with the excitation line of 514 nm. Analyses of SERS data over the potential region from 0.5 to −0.3 V enabled to obtain potential dependent adsorption isotherms, from which the formal redox potential could be estimated to be ca. −0.2 V. Up-tilted orientation of FePP SAM on Pt film electrode involving one peripheral propionate group attached to the surface and one propionic acid group hydrogen-bonded with adjacent FePP, was deduced based on in situ ATR-SEIRAS results, without significant structural change over the potential region from −0.1 to 0.9 V.

Key words: SERS; SEIRAS; iron protoporphyrin IX; SAM; Pt electrodes
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Introduction

Surface-enhanced vibrational spectroscopies can provide valuable structural information of adsorbates on electrode surfaces. In the past two decades, the instrumental advancement of Raman spectrometers, the improved surface-roughening, and the delicate design of core-shell nanostructures have enabled to extend the application of electrochemical surface-enhanced Raman spectroscopy (SERS) from traditional coinage metals to Pt-group and iron-triad metals[1]. Meanwhile, the new development of facile chemical and electrochemical depositions of various metallic films on Si windows has also made it possible to expand the scope of interfacial phenomena as probed by in situ surface-enhanced IR absorption spectroscopy (SEIRAS)[2].

Irreversibly adsorbed layers, mostly alkanethiol self-assembled monolayers (SAMs) on gold and silver surfaces have been intensively studied by surface-enhanced vibrational spectroscopies[3]. Recently, new focus of study has been directed on these SAMs on Pt-group and Fe triad metal surfaces due to their potential applications in manipulating corrosive and catalytic properties of the underlying metals[4-6]. Metalloporphyrin molecules can also form SAMs on metals, among them, iron protoporphyrin IX (simplified as FePP hereafter) has attracted an intensive interest due to its important role in biologically mimetic and electrocatalytic reactions. In fact, SERS[7-8] and ATR-SEIRAS[9-10] have been used to investigate the redox behavior of FePP SAMs on Ag[7-8], as well as the adducting of CO and NO ligands to FePP SAMs on Au[9-10]. While SERS is suitable for detecting the skeletal vibrations of FePP SAMs, SEIRAS is useful

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for detecting polar ligands and peripheral groups of FePP SAMs.

In order to further extend these two vibrational spectroscopies to non-traditional SAMs-modified electrodes, in the present work, we preliminarily report the electrochemical and structural information for FePP SAMs on Pt electrodes as revealed with *in situ* SERS and ATR-SEIRAS.

1 Experimental

SERS-activation of a Pt electrode was realized with the so-called square-wave oxidation reduction cycles in 0.5 mol · L^{-1} H_2SO_4 according to a previous report[11]. The self-assembly of iron (III) protoporphyrin IX ($Fe^{III}PP$) (Aldrich Chemical Co.) adlayers was achieved by immersing the SERS-active roughened Pt electrode in 50 μmol · L^{-1} $Fe^{III}PP$-containing 0.1 mol · L^{-1} borax solution overnight. Raman spectra were taken on a confocal Raman microprobe system (LabRam II, HORIBA Jobin Yvon) equipped with a 514 nm Ar^+ laser and an air-cooled CCD detector. The microscope attachment was based on an Olympus BX40 system with a long working-distance (8 mm) lens (50 ×) objective. The laser beam impinged on the surface at an incident angle of ca. 90° and the scattered light was collected by the microscope in the 180° backscattering geometry. A 1800-grooves/ mm grating, a slit width of 200 μm and a pinhole of 600 μm were selected, yielding a spectral band pass of approximately 2 ~ 4 cm^{-1}. The radiation power on the electrode surface was about 1.5 mW, and the total acquisition time for each spectrum was 300 s.

The SEIRA-active Pt electrode was prepared according to the so-called two-step wet process in which a 60-nm-thick Au underfilm was first chemically deposited on the reflecting plane of a hemicylindrical Si prism followed by an electrodeposition of a pinhole-free 6-nm-thick Pt overfilm[2]. *In situ* ATR-SEIRA spectra were obtained by using Magna-IR E. S. P. System 760 FT-IR (Nicolet) with an unpolarized infrared radiation at an incidence angle of 65° with a spectral resolution of 4 cm^{-1}. All the spectra were shown in the absorbance unit defined as $-\log(I/I^0)$, where I and I^0 represent the sample (with FePP SAMs) and reference (without FePP SAMs) single-beam spectra at the corresponding potentials, respectively. Spectral analysis was carried out with the Grams 32 software package (Galactic, Inc).

Potential control was achieved with a ZF-3 potentiostat (Fangzheng Instruments, Shanghai) or a CHI660B electrochemistry workstation (CH Instruments, Shanghai). A platinum sheet and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively. All the measurements were run at room temperature. The potentials reported here are quoted with respect to SCE.

2 Results and Discussion

Fig. 1 shows the cyclic voltammograms of a roughened Pt electrode before (solid line) and after (dotted line) FePP SAMs modification in 0.1 mol · L^{-1} $HClO_4$ within the hydrogen adsorption and desorption potential window. It could be seen that the presence of $Fe^{III}PP$ SAMs decreased the surface Pt sites available for H electrosorption.

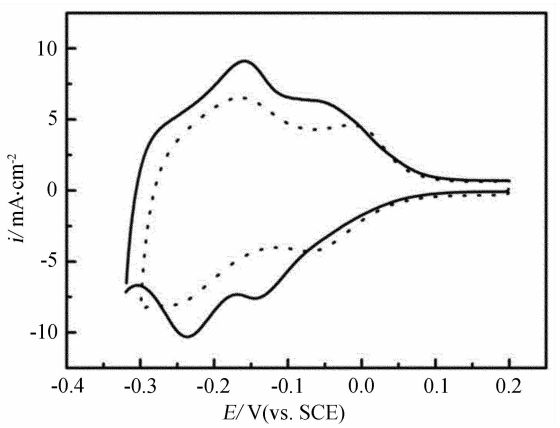

Fig. 1 Cyclic voltammograms for a Pt electrode before (solid line) and after (dotted line) being modified with FePP SAMs in 0.1 mol · L^{-1} $HClO_4$ at 100 mV · s^{-1}

Fig. 2 shows series of potential dependent SERS spectra for FePP SAMs on Pt electrode in 0.1 mol · L^{-1} $HClO_4$, collected stepwisely from 0.5 to −0.3 V, the corresponding band assignments are listed in Tab. 1. The bands at 1566 (ν_2), 1487 (ν_3) and 1624

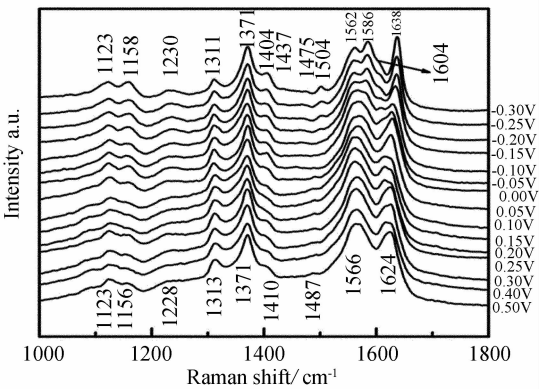

Fig. 2　Potential dependent SERS spectra of FePP SAMs on Pt electrode in 0.1 mol · L^{-1} $HClO_4$ with 514 nm excitation line, acquisition time: 300 s

cm^{-1} (υ_{10}) at 0.5 V are characteristic of μ-oxo form of Fe^{III} PP[7]. During the negative going potential movement to −0.3 V, the υ_2, υ_3 and υ_{10} bands shifted to 1562, 1504 and 1638 cm^{-1}, respectively, indicative of a decrease in the core size of the porphyrin skeletal ring, probably due to the potential induced transformation of the high-spin five-coordinated Fe(III) state to the intermediate-spin four-coordinated Fe (II) state[7]. It was reported that lowering solution pH to 3 caused the collapse of dimeric μ-oxo Fe^{III}PP to monomeric Fe^{III}PP on Au and Ag electrodes[7], however, here the dimeric μ-oxo Fe^{III}PP appeared rather stable on the Pt electrode even at pH 1 at relative positive potentials. Specifically, the 1487 cm^{-1} feature kept largely unchanged from 0.5 V to 0.05 V, whereas the monomeric Fe^{II} PP feature, i.e., the band at 1504 cm^{-1} showed up only at potentials more negative than 0.05 V.

Unlike on carbon electrode, no clearly discernable voltammetric features associated with changes in redox state could be observed for FePP SAMs on Pt electrode. The central metal oxidation-state marker, i.e., the υ_3 band at 1504 cm^{-1} for the reduced state (Fe^{II}PP) was taken to estimate the formal potential of the FePP on Ag at pH 3[7], yielding a value of −0.23 V. In addition, the band around 1311 cm^{-1} could be used to normalize the intensity variation due to the inhomogeneous SERS effect across the Pt surfaces. From the peak position of the derivative curve of the isotherm (approximately

Tab. 1　Peak frequencies (cm^{-1}) and assignments for selected vibrations of iron protoporphyrins on Ag, Pt and in solution

	modes	[a]μ-oxo-Hemin pH 9.8	[b]μ-oxo-Hemin CH_2Cl_2	[c]SERS Ag pH 3		SERS Pt pH 1	
				Fe(III)	Fe(II)	Fe(III)	Fe(II)
υ_{10}	$B_{1g(Ca-Cm)}$	1616	1622	1628	1640	1624	1638
υ_{37}	$E_{1u(Cb-Cb)}$		1585	1586	1587	undetected	1586
υ_2	$A_{1g(Cb-Cb)}$	1560	1568	1570	1565	1566	1562
υ_3	$A_{1g(Ca-Cm)}$	1480	1489	undetected	1504	1487	1504
υ_{20}	A_{2g}						
υ_{29}	$B_{2g(Ca-N)}$				1407	1410	1404
υ_4	$A_{1g(Ca-N)}$	1363	1371	1372	1372	1370	1371
υ_{21}	$A_{2g\delta(CH2)}$	1300		1311	1311	1313	1311
υ_{30}	$A_{2g\upsilon(Cb-Ca)}$	1158	1167	1168	1163	1156	1160
$\upsilon_6+\upsilon_8$	A_{1g}	1118		1128	1127	1123	1123

a. Data obtained in our laboratory for 50 μmol · L^{-1} FePP dissolved in 0.1 mol · L^{-1} borax solution. Excitation line 514 nm.

b. Data from Refs. [Sanchez et al. J. Phys. Chem. 89, 763, (1985)].

c. Data from Refs. [Cai et al. J. Electroanal. Chem. 524-525, 36, (2002)].

represented by the percentage plot of the $Fe^{II}PP$ spectral contribution as a function of potential) as shown in Figure 3, the formal potential was roughly determined to be ca. −0.20 V for FePP SAMs on Pt electrode in 0.1 mol · L^{-1} $HClO_4$.

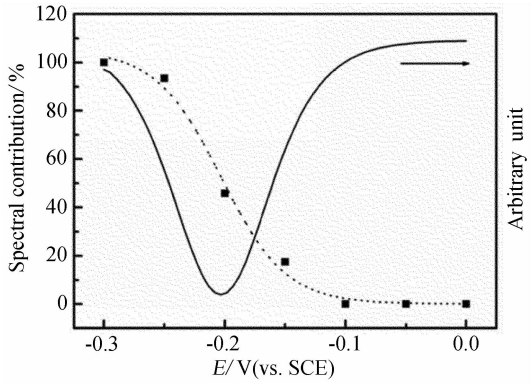

Fig. 3 Plots of the percentage of the spectral contribution of the 1504 cm^{-1} band from $Fe^{II}PP$ as a function of potential
the peak-shaped curve represents the derivative of the adsorption isotherm (solid line) obtained from best fits to the experimental data (dashed line)

The surface enhancement factor is an important parameter for this type of functional electrode, which can be evaluated according to the formula below[12]:

$$G \approx \frac{hcN_A\sigma I_{surf}}{RI_{bulk}} = \frac{21cN_A\sigma I_{surf}}{RI_{bulk}} \quad (1)$$

where c is the bulk concentration of the analyte FePP in solution; N_A is the Avogadro's constant; σ is the surface area occupied by a unit of μ-oxo $Fe^{III}PP$ (ca. 1.04 nm^2)[13], h is the height of waist of a focus laser beam in the bulk solution, which is about 21 μm for a pinhole size of 600 μm; R is the roughness factor of the Pt surface; I_{surf} and I_{bulk} is the integrated intensity of one vibrational band of FePP on Pt and in bulk solution, respectively. From Fig. 4, the ratio of the v_4 band intensity for $Fe^{III}PP$ on Pt and in solution can be obtained, thus the surface enhancement factor of $Fe^{III}PP$ on Pt was estimated to be about 40. This low value seemed insufficient to yield good-quality surface Raman spectra, therefore, surface roughness factor and weak resonant Raman effect for FePP with the 514 nm excitation line should contribute to the much larger overall enhancement.

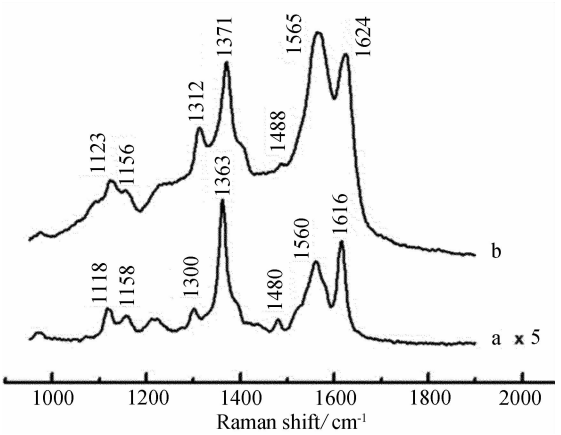

Fig. 4 Raman spectrum of 50 μmol · L^{-1} FePP in 0.1 mol · L^{-1} borax (a) and SERS of FePP on Pt in 0.1 mol · L^{-1} $HClO_4$ (b) with an acquisition time of 300 s

In order to provide complementary structural information for FePP SAMs on Pt electrode, SEIRAS was also applied to determine the orientation of FePP SAMs on Pt electrode. Fig. 5 shows series of potential dependent SEIRAS of the FePP/Pt in 0.1 mol · L^{-1} $HClO_4$, collected stepwisely from 0.1 to 0.9 V with the reference spectra taken for the bare Pt electrode under otherwise same conditions. The peaks at 1716, 1388, 1438 and 1639 cm^{-1} can be attributed to the C═O stretching vibration mode of hydrogen-bonded—COOH, the symmetric stretching mode of $—COO^-$, the C—H deformation of short alkyl chains and the scissoring vibration mode of interfacial H_2O[14], respectively. The two peaks around 2900 cm^{-1} are due to the CH_2 stretching modes. However, the antisymmetric stretching mode of the carboxylate group gave no resolved band that usually appeared in the 1500 ~ 1600 cm^{-1} region, suggesting that the carboxylate group is bound to the Pt electrode in a symmetric geometry.

Different from FePP SAMs on Au electrode[9-10], the frequencies and intensities for the δ_{CO} and v_{OCO} bands were largely unchanged with the potential. The hydrogen-bonded —COOH of FePP may explain the rather stable adsorption over the potential range from 0.1 to 0.9 V. According to surface selection rule, the short CH_2 chain is tilted with respect to the metal surface, as evidenced by the appearance of CH stretch

bands in the 3000 ~ 2800 cm^{-1} region. Therefore, it may be proposed that the porphyrin plane is tilted to a local Pt surface with its peripheral propionate group attached to the surface through the bridge configuration, with its peripheral propionic acid group interacted with neighboring molecules through hydrogen bonding[14].

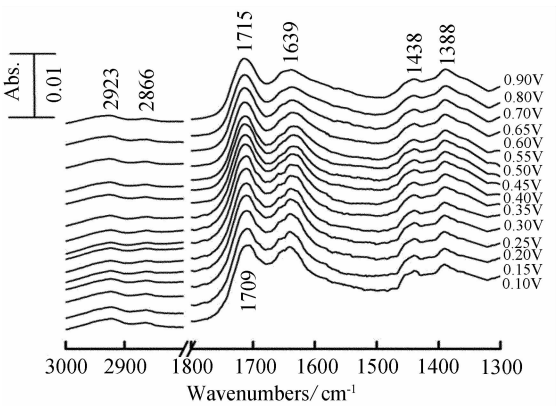

Fig. 5　Potential dependent ATR-SEIRA spectra for a FePP/Pt electrode in 0.1 mol · L^{-1} $HClO_4$ (reference spectra and sample spectra were taken before and after FePP adsorption)

3　Conclusions

Electrochemical and structural properties of FePP SAMs on Pt electrodes in 0.1 mol · L^{-1} $HClO_4$ have been initially investigated with *in situ* SERS and ATR-SEIRAS. Analyses of SERS spectral data, specifically, the potential dependent intensity variation of an oxidation state marker, or the ν_3 band, enabled the formal redox potential of FePP SAMs to be estimated to be ca. −0.2 V. Up-tilted orientation of FePP on Pt electrode was assumed based on *in situ* ATR-SEIRAS data with a nearly unchanged configuration, involving one peripheral propionate group attached to the surface, and one propionic acid group hydrogen-bonded with other molecules.

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铂电极上自组装铁原卟啉单分子层的表面增强振动光谱初探

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摘要: 应用现场表面增强拉曼光谱和衰减全反射表面增强红外光谱初步研究了 0.1 mol · L^{-1} $HClO_4$ 溶液中 Pt 电极表面铁原卟啉(FePP)自组装单层的电化学和结构特性. 以 514 nm 波长为激发线,得到了增强因子约为 40 的粗糙 Pt 电极上 FePP 在不同电位下的表面增强拉曼光谱. 分析 0.5 ~ −0.3 V(SCE)区间内谱峰变化,得到近似的吸附等温式,由此可估算出 Fe^{3+}/Fe^{2+} 的式量电位大约为 −0.2 V. 原位表面增强红外光谱的测试结果表明,FePP 分子主要以斜立方式吸附在 Pt 膜电极表面,其中一个环外羧酸根与电极表面相接触,而另一羧酸基团以氢键与相邻的 FePP 分子相连. 这样的吸附结构在 −0.1 ~0.9 V(SCE)的电位区间内并没有显著的变化.

关键词: 表面增强拉曼光谱; 表面增强红外光谱; 铁原卟啉; 自组装单分子层; 铂电极