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## Confocal Microprobe Raman Spectroscopy for Investigating the Electrochemical Interface

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**Detailed abstract:** The invention of the surface enhanced Raman spectroscopy (SERS) in the mid of 1970s, opened an entirely new and very promising area. However, it was found that SERS of practical application in electrochemistry can only be found on noble metal surfaces, such as Ag, Au and Cu that exhibit huge surface enhancement<sup>[1]</sup>. This greatly limits the application of SERS in electrochemistry. In electrocatalysis, corrosion inhibition, sensor, and power source, the most widely used materials are Pt, Fe and Ni and their alloys as well as Si. Thus, it is of great significance to extend surface Raman study to transition metals and semiconductors. Although the effort has been made along this direction by several groups since the late of 1970s, only recently, this goal has been attained<sup>[2,3]</sup>.

The success of our work towards the goal is benefited from the improvement of the Raman instrumentation and the development of proper electrode surface pretreatment for transition metal surfaces. The employment of the charge-coupled device (CCD) detector, the confocal microscope, and the notch filter in the Raman instrumentation, brought up a new generation Raman instrument. It provides very high sensitivity that can partially break the limitation of the sensitivity to the surface Raman investigation<sup>[4]</sup>. The most important is, with the confocal pinhole, the instrument can only collect the light from the focus of the laser, thus it can effectively exclude the interference of the solution Raman signal, which makes the detection of very weak Raman signal from surface feasible. The emphasis of this paper is placed on the methodology. Some examples

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are given to demonstrate the advance in this area.

## 1 Spectroelectrochemical setup

A spectroelectrochemical cell with a proper design is crucially important to the Raman study. On one hand, it should have a minimum loss of the signal. On the other hand it should retain the electrochemical reaction. Fig. 1 gives the spectroelectrochemical cell designed to fit for the working condition of the LabRam I confocal microprobe Raman system. The Raman system utilizes a backscattering configuration to collect the Raman signal through a microscope vertically. Thus, a spectroelectrochemical cell with the electrode facing up is needed. In this configuration, the evaporated solution, as well as the product generated during the electrochemical process will contaminate the microscope objective right above the electrode as well as the instruments, which might lead to the etching of the lens and result in the degradation of the throughput of the system. To overcome this problem, the cell was designed with a quartz or glass cover to form a closed system. This system has triple functions: First, to isolate the solution from the microscope objective to prevent the etching of the objective by the solution. Secondly, to eliminate the possible contamination from the air to the electrochemical system. Thirdly, with a proper holder, the cell is capable of standing up with the electrode surface facing vertically or lying down with the electrode surface facing up. Furthermore, the cell is capable of serving as a flow cell or purging gas during the experiment with proper adapters. In the case that extremely weak signal is to be detected, a kind of thin transparent and colorless plastic film is employed to wrap the objective to avoid the damage of the electrolyte to the microscopic objective. The signal loss by this tactic is only about 20% compared with the 50% loss using a quartz window. This tactic is very important for the in situ study of the etching process of the silicon surface in HF, in which the HF could etch the quartz window and the microscopic objective. The disadvantage of this method is that this kind of configuration will very easily introduce the contamination from the air. However, it is a very successful tactic if the system studied is not very sensitive to the contamination for the ambient air.

are given to demonstrate the advance in this area.

## 2 Surface roughening procedure for Pt electrodes

The surface roughening procedure has been introduced in detail in Ref. 5, the surface roughness factor can be calculated by comparing the charge flowing in the hydrogen region, i.e.,  $R = Q_{\text{rough}}/Q_{\text{smooth}}$ , where the  $Q_{\text{rough}}$  and  $Q_{\text{smooth}}$  can be obtained from the corresponding cyclic

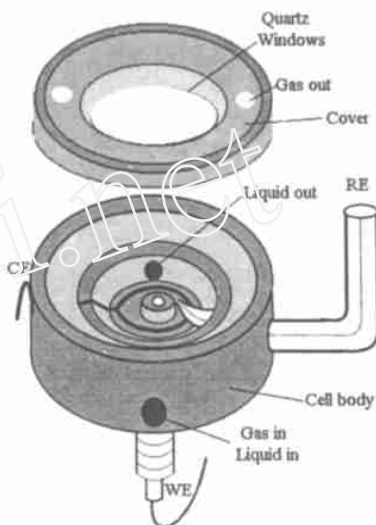


Fig. 1 Electrochemical Raman cell for the confocal raman system

voltammograms of smooth and roughened Pt electrodes. Although longer roughening time leads to a larger surface area, the Raman intensity is not proportional to the surface area. A very important point should be mentioned here is the Pt electrodes have to be very carefully polished, especially those have already been subjected to an extensive roughening. The incomplete polishing will result in the failure during the next roughening.

The STM image of a highly roughened Pt surface (with  $R = 200$ ) is given in Fig 2. It could be found that the Pt surface presents very rough but quite uniform structure. Humps about 200 nm is present. Zooming the image into a smaller range, some fine structures around 10 to 20 nm on the 200 nm humps can still be found. This may give the evidence for the large enlargement of the surface area.

It should be noted that, the roughened Pt shows very good stability and reversibility after the extensive surface pretreatment. More interestingly, the Raman signal could be recovered completely upon returning the electrode potential to a more positive value after a very negative potential excursion. The most exciting is the electrode can be reused over a long time as long as it is subject to an electrochemical cleaning procedure by cycling in a  $H_2SO_4$  solution previous to each new experiment. It was found that the SERS from this surface is quite uniform. The above advantages ensure the vibrational properties of the adsorbate probed by surface Raman spectroscopy to be reasonably representative of those for the entire surface rather than some SERS active sites. Accordingly, this development in surface Raman spectroscopy may further prove it to be a general and reliable technique with the capability of more wide and practical applications.

On this kind of Pt surface, we have obtained high quality Raman signal of the adsorbed pyridine, and the surface enhancement factor was estimated to be around  $100^{[6,7]}$ . Our success in obtaining the surface Raman signal from Pt surfaces greatly encourages us to extend the surface Raman study to other transition metal surfaces, such as Ni, Fe, Co, Ru, Rh and Pd, which has also proved to be very successful<sup>[3,5-7]</sup>. In this paper, the coadsorption process on the Pt surface, and a unique method for calculating the solution pH are also introduced.

### 3 To probe the coadsorption process and identify the surface species

With the stable and reversible SERS substrate, one is able to investigate a roughened platinum electrode in an HCl solution in a wide potential range. Fig. 3(a) gives the cyclic voltammogram of the roughened Pt electrode in 1 mol/L HCl. It can be seen that there are two desorption

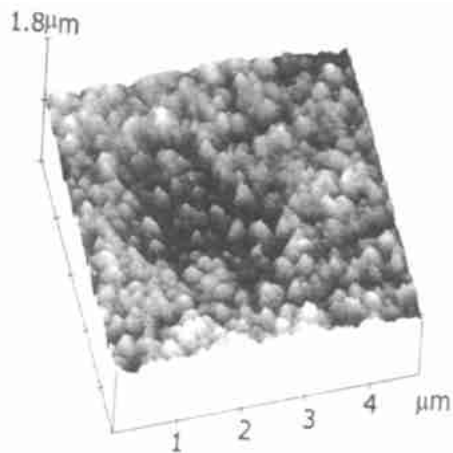


Fig. 2 STM image of a roughened Pt electrode surface with roughness factor about 200

and three adsorption peaks, which include the adsorption and desorption of  $\text{Cl}^-$ . Hydrogen evolution initiates at  $-0.25\text{ V}$ , and becomes significant at  $-0.3\text{ V}$ . The adsorption of oxygen is evident at  $0.7\text{ V}$ . Fig. 3(b) gives the corresponding surface Raman spectra from the Pt electrode in  $1\text{ mol/L HCl}$ . At very negative potential, a broad band at  $2082\text{ cm}^{-1}$  can be found, this band can still be seen at  $-0.25\text{ V}$  at the starting potential of the hydrogen evolution. Further positive moving of the potential into the hydrogen underpotential deposition region, no band related to the underpotential deposited hydrogen can be found, as well as that related to  $\text{Cl}^-$ . When the potential was moved into the strongly bound hydrogen evolution region, a band at  $295\text{ cm}^{-1}$  emerges, whose frequency blue shifts with the positive going of the electrode potential. This behavior, together with the previous data obtained in platinate chloride compounds, encourages to us to assign this band to the Pt-Cl vibration. This band shift quite dramatically with the positive movement of the potential. A Stark effect value  $d/dE$  was estimated to be about  $65\text{ cm}^{-1}/\text{V}$ . Interestingly, at  $0.70\text{ V}$ , where in the CV the oxygen adsorption commences, we observed a new broad band at ca.  $560\text{ cm}^{-1}$ , which has been assigned to the oxygen-containing species at the Pt surface in our previous study of other systems. The ability of detecting three distinctly different Raman signals originating from different species at the electrode surface demonstrates convincingly the merit of Raman spectroscopy. From the result, we could characterize the interaction between different species on the surface and their interaction with the surface. It is evident that both hydrogen and chloride interact strongly with the platinum surface, but the existence of hydrogen resists the  $\text{Cl}^-$  from adsorption. This behavior could be described as a competitive adsorption. While for  $\text{Cl}^-$  and oxygen, they can also interact strongly with Pt, but they can coexist at the electrode surface in a certain potential range. Raman spectroscopy in itself not only presents its advantage in analyzing the adsorbate and substrate interaction, but also behaves as a powerful tool to identify

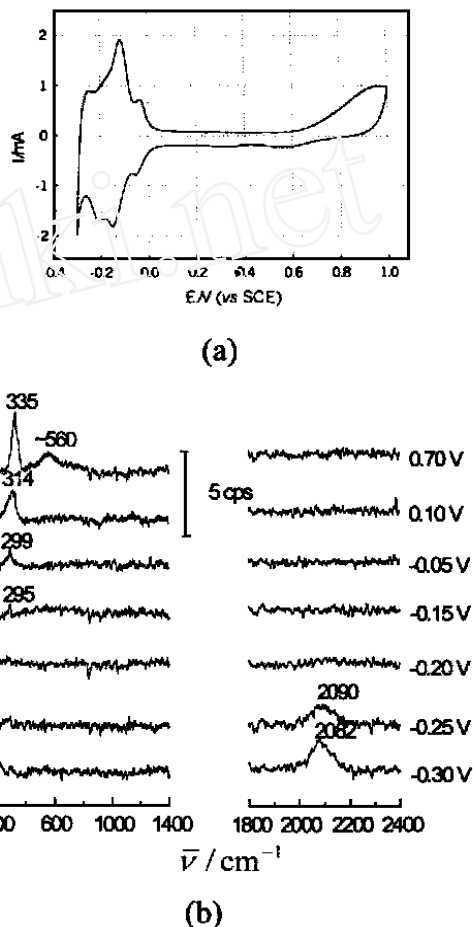
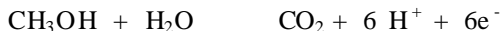


Fig. 3 (a) Cyclic voltammogram of a Pt electrode in  $1\text{ mol/L HCl}$  solution and (b) the corresponding potential dependent surface Raman spectra.

the behavior of the surface species.

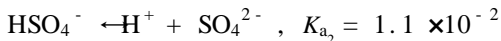
#### 4 To detect the concentration profile and estimate the solution pH

Compared with the conventional Raman spectroscopy, confocal Raman spectroscopy has much higher sensitivity to detect the solid/liquid interfacial structure and has a very high vertical resolution, because only the signal from the laser focus can be detected by the system, the signal from other plane of the solution is discriminated by the pinhole. This ensures the eliminating of the signal from the bulk solution. Thus, we could focus the laser at different layers of the solution by moving the X-Y stage vertically to perform layer analysis, i. e., change the distance ( $d$ ) between the laser focus and the electrode surface, to detect the concentration gradients of this solution. Fig. 4 gives a good example. 1 M methanol in 0.1 M sodium sulfate was served as the test solution, and the potential of the Pt working electrode was held at 0.9 V where severe methanol electrooxidation occurs. As can be found from the figure that, with the decrease of the distance, the peak at  $1018\text{ cm}^{-1}$  corresponds to the C-O vibration of the methanol decreases as the result of the severe electrooxidation of methanol in the vicinity of the electrode surface. Meanwhile, the change could also be found on the relative intensity of the peaks at  $980$  and  $1050\text{ cm}^{-1}$  corresponding to the vibration of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  in solution, respectively. This could be well explained by the electrooxidation mechanism of methanol in this solution, where



Thus, it is expected that the oxidation of methanol will substantially increase the concentration of  $\text{H}^+$  near the surface, hence decrease the solution pH. A hint from study is that we can use the relative intensity change of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  to calculate the solution pH. The detail will be given as follows.

In the sulfuric acid solution, the following equilibrium exists,



Now defining the concentration of the sulfate ion as  $C_{\text{SO}_4^{2-}}$ , according to the following equation,

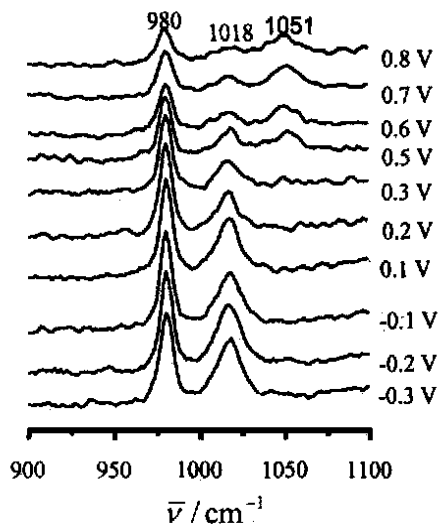


Fig. 4 The Raman spectra of solutions in interfacial region changed with the change of the electrode potential. Solution: 1 M methanol + 1 M  $\text{Na}_2\text{SO}_4$

$$K_{a_2} = \frac{C_{\text{SO}_4^{2-}} \cdot C_{\text{H}^+}}{C_{\text{HSO}_4^-}}, \quad (1)$$

we could define  $C_R = \frac{C_{\text{HSO}_4^-}}{C_{\text{SO}_4^{2-}}}$ , thus,

$$C_{\text{H}^+} = K_{a_2} \cdot C_R \quad (2)$$

From the Raman spectra, we could get the ratio of the integrated intensities of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  peak, which could be presented as  $I_R = I_{\text{HSO}_4^-} / I_{\text{SO}_4^{2-}}$ . In a medium concentration, the Raman signal from the solution species is thought to have a linear relationship with the concentration. Thus,

$$I_{R_1} / I_{R_2} = C_{R_1} / C_{R_2}, \text{ i. e. , } I_{R_1} / I_{R_2} = C_{(\text{H}^+)_1} / C_{(\text{H}^+)_2}$$

After obtaining the  $I_{R_1}$  from the solution Raman spectra, and the known pH value of the bulk solution, with the  $I_{R_2}$  obtained in the desired region, one can calculate the  $C_{\text{H}^+}$  by equation 2 hence the solution pH. This provided a unique way to calculate the solution pH by Raman spectroscopy. Thus the confocal microprobe Raman system provides quite a sensitive way to do the solution concentration profile.

The above study clearly shows that with the help of the high sensitive Raman instrument, proper design of the experiment and the appropriate surface pretreatment procedure, one could successfully extend Raman spectroscopy to transition metal surfaces. We have also successfully obtained signals from other transition metal surfaces, such as Fe, Ni, and Rh, as well as semiconductor Si surface. This will inevitably deepen our understanding of the SERS phenomenon and develop Raman spectroscopy into a general, powerful and versatile tool for analyzing the interfacial structures.

**Key words:** Electrochemical interface, Confocal microprobe Raman spectroscopy, Platinum, Roughened, Coadsorption

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# 用于电化学界面研究的共焦显微拉曼光谱技术

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**摘要:** 系统地介绍了将共焦显微拉曼光谱系统用于电化学界面研究的方法, 包括铂电极的粗糙和电化学拉曼电解池的设计. 进行了铂上氢、氧和氯共吸附的拉曼光谱研究. 通过对甲醇氧化过程的现场跟踪, 提出检测界面区溶液浓度变化和计算溶液 pH 值的方法. 实验表明拉曼光谱技术可作为研究实际应用体系的重要工具.

**关键词:** 电化学界面; 共焦显微拉曼光谱; 铂; 粗糙; 共吸附