Account

Molecular-level investigation on electrochemical interfaces by Raman spectroscopy

TIAN, Zhong-Qun*(田中群)   REN, Bin(任斌)

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Institute of Physical Chemistry, Xiamen University, Xiamen, Fujian 361005, China

The structure and dynamics of electrode/liquid interfaces play an increasingly important role in electrochemistry. Raman spectroscopy is capable of providing detailed structural information at molecular level and new insight into the interfacial structure, adsorption, reaction, electrocatalysis and corrosion. In this account we will summarize some progresses of surface Raman spectroscopy in the study of electrochemical interfaces, mainly based on our group's work, laying emphasis on the detection sensitivity, spectral resolution, time resolution and spatial resolution as well as the hyphenated technique.

Keywords   Raman spectroscopy, surface enhanced Raman spectroscopy, electrochemical interfaces, adsorption

Introduction

The structure and dynamics of electrode/liquid interfaces play an increasingly important role in electrochemistry. The ramifications of the subject extend into diverse areas such as battery, fuel cell, material corrosion, clean technology, semiconductor processing, electric synthesis of organic and inorganic compounds, conversion and storage of solar energy, and biological electron transfer process. Traditional electrochemical methods can not meet the growing requirement of characterizing more complicated systems related to advanced materials and life science.[1] Since 1980s there have been remarkable developments of non-electrochemical techniques, particularly *in-situ* spectroscopies, diffraction techniques and scanning probe microscopes (SPM) to gain more mechanistic and dynamic information from electrochemical interfaces at the molecular (atomic) level.[2-4] It is necessary to point out that each individual technique has some advantages and disadvantages in the study of a certain electrochemical system. Generally, the detection sensitivity and resolution are the two most important criteria for comparing these techniques in terms of their capability to obtain more information from the interface. The resolution can further be classified into three factors, *i. e.* energy-resolution, spatial-resolution and time-resolution. The detection sensitivity is absolutely important because only an extremely small quantity of species providing meaningful information are present in the interface in comparison with the bulk solution phase. The electrochemical technique has very high sensitivity capable of detecting a change of sub-monolayer molecules or atoms at the interface. However, it has quite poor time resolution of milliseconds unless one uses ultramicroelectrodes to reach the resolution up to microseconds.[5] Moreover, its energy-resolution is even poor at around 10^{-2} V. In contrast, *in-situ* vibrational spectroscopies such as Raman and IR spectroscopies have much higher energy-resolution, their spectral resolution is *ca.* 1 cm^{-1}, which is equal to about 10^{-4} eV. Therefore, the vibrational spectroscopies are capable of providing detailed structural information and new insight into variety of electrochemical interfaces.[2,3] In this account we will summarize some progresses of surface Raman spectroscopy in the study of electrochemical interfaces, mainly based on our group's work, laying emphasis on the detection sensitivity, spectral resolution, time resolution and spatial resolution as well as the hyphenated technique.

Detection sensitivity

Detection sensitivity to probe electrochemical interfaces has always been the key problem for the optical method due to the fact that only one monolayer or even sub-monolayer of the interested species are presented at the interfaces. Laser Raman spectroscopy itself has been suffering from the intrinsic low detection sensitivity. Fortunately, in 1978, it was largely discovered through the work of Fleischmann, Van Duyne, Creighton, and their co-workers that molecules adsorbed on specially prepared silver surface produce a Raman spectrum, in which the signal intensities at times increase million fold than expected. This effect was dubbed surface enhanced Raman scattering(SERS).[6-8] The following examples illustrate that the very high sensitivity to surface adsorbed species makes it possible to use surface enhanced Raman spectroscopy to investigate electrochemical interfaces in detail.

Interfacial water molecules

The interfacial water as the major component of electrode/aqueous electrolyte interfaces is one of the most important subjects in fundamental electrochemistry, and its detailed structure and behavior are far from a consensus recognition. SERS seems to be a powerful tool for investigating the structure of interfacial water because it can greatly enhance the Raman signal of interfacial water molecules and avoid tremendous interference of bulk water (about 55 mol/L). However, the extensive study in the 1980s showed that SERS of water was only obtained under some special conditions, i.e., the solution must contain (pseudo-) halide salts.[9-11] The results imply that the SERS arises from special surface complexes involving metal adatoms, halide ions, cations and water molecules. Therefore, it is questionable that to what extent the water molecules present at these surface complexes are representative of normal water present at electrode/electrolyte interfaces. In consequence the SERS study on water declined considerably at the end of 1980s.

In the early 1990s we collaborated with Funtikov's group and successfully obtained the SERS of water in a $NaClO_4$ solution free of (pseudo-) halide ions in a wide potential range, e.g. from -0.5 V to -2.0 V.[12] By taking advantage of high sensitivity and high spectral

resolution of SERS, we carried out the systematic study on the effects of electrolyte ion (Li^+, Na^+, K^+, Cs^+, ClO_4^-, SO_4^{2-} and OH^-),[13] electrode substrate (Au, Ag and Cu)[14,15] and potential on the SERS features of water. Fig. 1 shows a set of surface enhanced Raman spectra of H_2O from an Au surface changing with the electrode potential. It is of special interest to find that in the potential region of hydrogen evolution reaction (noted as H_2O (HER)), the spectral feature is strikingly different from that in the double layer potential region. The libration and bending band intensities of H_2O (HER) are abnormally enhanced in comparison with the stretching mode. Based on the fact that the strong libration band of water can only be obtained from solid state like ice, one could assume that the H_2O (HER) may have highly ordered structure, thus to expedite the transfer of electron and OH^- and H^+ through the unique hydrogen bonding net in HER. More surprisingly, the SERS feature of H_2O (HER) is distinctively different from that of most surface species in SERS study. Its intensity is well proportional to the electrochemical reaction rate (i.e., the current of HER) but is independent on Ag, Cu, and Au surfaces, in spite of the fact that the potentials of zero charge (PZC) for these metals are very different. We have also found that the surface enhancement factor (SEF) of water at the HER potentials is estimated to be ca. 10^6 while in the double layer potential region the SEF is only ca. 10^4.[14] Accordingly, the new enhancement mechanism is suggested by the correlation of HER current density and the SERS intensity during the course of electrochemical dissociation of interfacial water molecules. It may involve the charge transfer (CT) from the metal to the activated intermediate energetic state of those water molecules to be dissociated.[15]
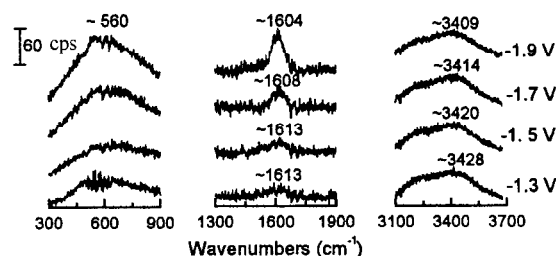

Fig. 1   SERS of water on an Au electrode in 0.1 mol/L Na_2SO_4 solution as a function of the electrode potential. Excitation line: 632.8 nm.

Transition metal surfaces

It should be pointed out that the huge surface enhancement effect was found to be severely restricted to three noble metals of Ag, Au and Cu. Thus surface-enhanced Raman spectroscopy has almost been restricted to these surfaces for over two decades. Therefore, it is fatally important to extend SERS study to other metallic and non-metallic surfaces. In particular, much effort has been devoted to the study of catalytically more interesting transition metals in the past decade.[9,16-20] However, due to the low detection sensitivity of Raman spectroscopy, no significant breakthrough has been made in this area. As a consequence SERS has not been used as widely as IR spectroscopy in surface science and electrochemistry.

Recently we have used a confocal Raman microscope (LabRam I, Dilor) with the very high sensitivity and special surface pretreatments to extend SERS study successfully to many bare transition metals of practical importance.[21-35] More than five surface pretreatment procedures for different transition metals have been examined, i.e., mechanical polishing, chemical etching, electrodeposition, ex-situ and in-situ electrochemical oxidation and reduction cycle(s) (ORC) etc. It has been found that the substantial increase in the signal intensity is not simply proportional to the surface roughness. Therefore, one should consider the actual SERS effect from these roughened surfaces. The surface enhancement factor (G) is defined as $G = \dfrac{I_{surf}/N_{surf}}{I_{bulk}/N_{bulk}}$, where I_{surf} and I_{bulk} denote the integrated intensities of the same band for the adsorbate at surface and in solution respectively, while N_{surf} and N_{bulk} represent respectively the number of the corresponding molecules effectively excited by a laser beam. Since the confocal Raman microscope possesses a sensitive depth resolution, as for a conventional Raman spectroscope the term N_{bulk} and N_{surf} can not be obtained directly. By considering the confocal optical feature, we proposed an approach to calculate the SEF of these metal systems and got one to two orders of amplification of surface Raman signal from Pt surfaces, and two to three orders from Ni and Fe electrodes.[25,29,31-33] The results demonstrate the importance of establishing the appropriate surface pretreatment procedure for obtaining SERS effect from the transition metals.[25,31,32]

It is of special interest to extend the study to the ordered nanorod (or nanowire) arrays of transition metals as a suitable SERS substrate. The arrays were fabricated by means of the templates of porous alumina with pore diameters between 10 and 40 nm. AC current was applied to deposit the metal into the pores. Then the alumina film was chemically etched off layer by layer by an aqueous solution of phosphoric acid, by which the metal nanorods or nanowires were exposed gradually at the surface, then SERS measurements were taken in sequence. It has shown that the SERS intensities depend critically on the rods' length exposed and are considerably stronger than that from the roughened electrode surfaces with the best preparation. For example, the surface enhancement factor of four orders for the Ni nanowire array can be obtained. It indicates that the ordered nanorod arrays could serve as a new class of SERS active substrates especially for transition metals.[34]

So far we have obtained good quality surface Raman spectra from many transition metal surfaces, such as Pt, Ni, Ru, Rh, Pd, Co, Fe and Pt(Ir) alloy electrodes, over a very wide electrode potential region (e.g. -2.0 V to +1.4 V); many important surface species, including the adsorption of CO, H, O, Cl⁻, Br⁻, SCN⁻, CN⁻, pyridine, thiourea, benzotriazole and pyrazine, have been investigated.[21-35] Fig. 2 gives two sets Raman spectra of inorganic and organic molecules adsorbed on some transition metal and alloy metal surfaces. To gain insight into the nature of the metal-adsorbate bonding, we have paid special attention to the vibrational bands reflecting the interaction between substrate and adsorbates, which is very difficult to be studied by other in-situ vibrational spectroscopy such as IR and SFG.[36,37] This demonstrates virtues of surface Raman spectroscopy for yielding information on surface bonding related to the surface coverage, coadsorbate and electrode potential.

For extending SERS to transition metals, another important tactic to electrochemically deposit "pin-hole free" transition metal thin films over SERS active Au surface has also been proposed recently by Weaver's group. They have successful extended Raman study to Rh, Ru, Ir, Pt and Pd surfaces. The surface species that have been investigated include CO, benzene, benzonitrile.[38,39] Very recently in the collaboration work of our two groups, the study has been further extended to thicker films which are more close to bulk transition metal in properties. High-quality surface Raman spectra of

the adsorption of SCN⁻ on Rh, H on Pt and Rh, CO on thicker film of Rh, Pt and Pd have been obtained for the detailed investigation.[40]
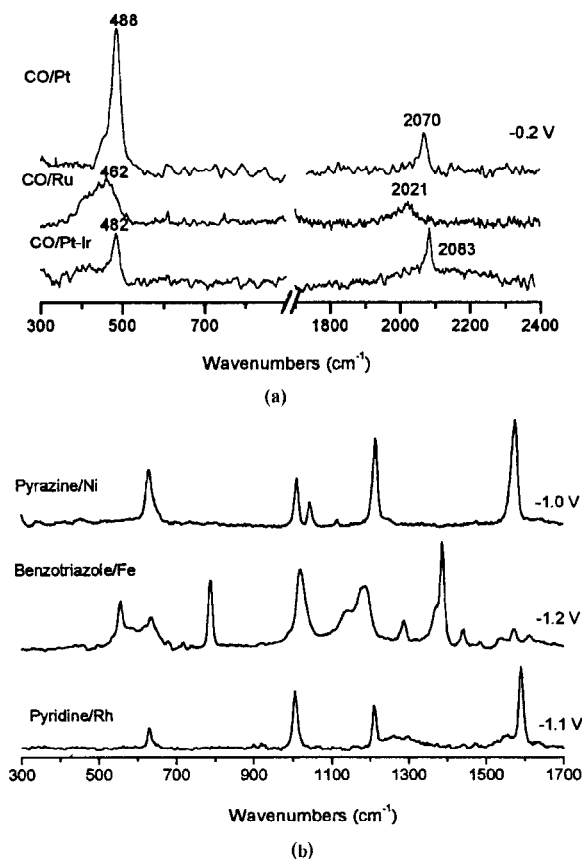

Fig. 2   Surface Raman spectra from various transition metal systems as indicated in the figures. Raman spectra were recorded in Labram I confocal microprobe Raman system, with either green (514.5 nm) and red (632.8 nm) laser excitation.

Non-metallic material surfaces

Another important direction of surface Raman spectroscopy is its application to non-metallic materials like semiconductor and conductive polymer electrodes, which are non-SERS active. The study can be realized by using either resonance Raman effect or surface enhanced Raman effect or their combination.[41] Xue's group has carried out a systematic study on the structure of polymer/metal interfaces in non-electrochemical environments by

covering the SERS active Ag surface with the thin polymer film.[42-44] They also developed a method to obtain SERS signal from non-SERS metal surfaces, by which the molecules investigated was adsorbed on those chemically etched surfaces, and then Ag particles were chemically deposited over them.[45,46] They have obtained SERS signal of various molecules on various surfaces,[47,48] which has been proved to be from substrates rather than silver surface. Our group, on the other hand, have focused on the structures of conductive polymers under electrochemical conditions, and several systems have been investigated, such as polyaniline and polypyrrole films, film/electrode interfaces and film/solution interfaces.[49-51] The SERS spectra can provide molecular level information for understanding the mechanisms of electropolymerization, electrochemical reaction and degradation of conductive polymer electrodes.[49-51]

Surface bonding configuration of silicon is a subject of extreme importance both for practical and academic reasons because it is correlated with silicon etching procedures and electro-optical properties. Using a highly sensitive confocal microprobe Raman system, we *in situ* studied Si—H$_x$, Si—F and Si—Si vibrations from Si electrode surfaces in HF aqueous solution.[31,51] Two approaches have been made for obtaining the best quality surface Raman spectra, *i. e.* by electrochemical roughening pretreatment or laser-assisted roughening procedure. The Raman scattering and photoluminenscence (PL) from the surface can be correlated. The result indicates the potential of confocal Raman microscopy as an important tool for *in-situ* investigating surface bonding configuration of semiconductor electrodes during the surface processing.

Energetic (spectral) resolution

As mentioned above, Raman spectroscopy can provide very high energetic resolution, which refers to the high spectral resolution in the word of spectroscopy. It is well known that different molecules could have different vibrational frequencies, even the same molecule with different surface configuration can be distinguished by Raman spectroscopy quite sensitively. With the aid of the extremely high sensitivity, SERS has the capability in detecting the mild change in both frequency and intensity of the surface species when it is slightly influenced by the environment, such as the applied poten-

tial, electrolyte ion or surface coverage.

Electrochemical coadsorption

Electrochemical coadsorption of organic molecules, inorganic ions and solvent molecules is a common yet complicated interfacial phenomenon. With its high spectral resolution, SERS can yield a detailed picture of coadsorption configuration.[53,54] Through carefully analyzing the potential dependent band feature including its frequency, intensity, width and shapes, one can classify the electrochemical coadsorption into two types—parallel (competitive) and induced coadsorption. Moreover, according to the frequency dependence of the induced coadsorbates on the electrode potential, we can further classify the induced coadsorption into two subtypes—induced physical coadsorption and induced chemical coadsorption.[53,54]

The first example of the induced coadsorption is that ClO_4^- or SO_4^{2-} ions can be induced to adsorb to the surface by some organic molecules, such as thiourea (TU).[53-55] Fig. 3 gives good example that demonstrates the induced coadsorption process. It has been found that the strong SERS signal from ClO_4^- can only be detected when TU is added. The band frequency of ClO_4^- is identical to that of free anions in electrolyte and entirely independent of the electrode potential. This phenomenon indicates that the anion is induced by the organic molecule to coadsorb at the electrode surface and it only interacts indirectly with the surface. It can be classified to be the induced physical coadsorption.[54] In order to analyze the coadsorption configuration, some SO_4^{2-} was added into the spectroelectrochemical cell. New SERS bands from SO_4^{2-} replace those of ClO_4^- completely, and meanwhile the band frequency from the NH_2 group of TU changes in several wavenumbers while the other bands of TU remain unchanged. This mild but meaningful change reveals that the coadsorption of TU with electrolyte anions is through the NH_3^+ group of TU.[55]

When the electrolyte anion is changed to SCN⁻ that can strongly interact with the surface, the potential dependent SERS study reveals that SCN⁻ and TU can be adsorbed individually or coadsorbed in parallel at the electrode surface. In the positive potential region, both the intensity and frequency of the coadsorbed SCN⁻ are different from those of the free anion in electrolyte or the individually adsorbed anion.[53] It infers that in the paral-

lel coadsorption, the interactions between the electrode surface and both kinds of adsorbate molecules are strong. It has also been found that the transition from parallel to induced coadsorption can be realized by changing the electrode potential toward the negative direction.[53] At the negatively charged surface, the desorption of SCN⁻ is preferred while TU can still interact with the surface strongly through its sulfur atom. So the adsorbed TU can induce the SCN⁻ to be coadsorbed to the surface due the strong interaction through the NH_3^+ group of TU and the nitrogen atom of SCN⁻. The results illustrate that the nature of the complicated potential dependent coadsorption can be understood at molecular level by analyzing the SERS spectra of coexistence of different kinds of surface species. More importantly, with the aid of rich structural information provided by Raman spectroscopy, quantum chemical calculation can be performed to elucidate the detailed nature of surface bonding, as shown in the hydrogen adsorption.
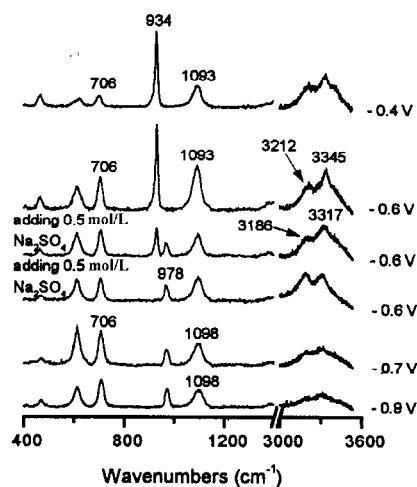

Fig. 3   SERS from the Ag surface of the coadsorption process of thiourea with SO_4^{2-} and ClO_4^- as a function of the electrode potential. Excitation line: 632.8 nm.

Hydrogen adsorption at platinum electrodes

Hydrogen adsorption at platinum electrodes is one of the most important systems known in electrochemistry. It has significance to many practical systems, such as fuel cell, water electrolysis, organic reduction and some corrosion processes. Though the interaction of Pt with hydrogen has long been a hot subject for electrochemists,

this seemingly simple system is by no means simple.[56] Hydrogen adsorption at platinum electrodes in acidic solution has been investigated by confocal microprobe Raman spectroscopy for the first time.[21,22,35] Vibration for on-top adsorbed hydrogen against platinum surface at ca. 2088 cm^{-1} is observed in the overpotential deposition (OPD) region of hydrogen evolution. With the negative moving of the potential, there is a red shift of Pt-H vibrational frequency. In the potential region of underpotential deposition (UPD) only a very weak and broad band is discernible when the surface hydrogens are saturated.[35] It indicates that the nature and bonding configuration of the surface hydrogen are remarkably different in the UPD and OPD regions. Several factors, including the applied potential, hydrogen surface coverage, interactions with electrolyte ions and water molecules, can influence the observed spectroscopic properties.

By considering the wealthy spectroscopic data, we performed *Ab initio* cluster model calculations. Electric field effects were simulated either by charging the cluster models or considering the cluster in the presence of a uniform external field. The calculation results indicate that the large tuning rate of Pt-H frequency should be attributed to the work function shift with the change of electrode potential, and the effect coming from the interaction between external electric field and the dipole moment of the adsorbate is considerably small. The calculation results show that the spectroscopic properties of Pt-H bond are very sensitive to the surface coverage. The observed red-shift of Pt-H frequency with decrease of electrode potential would originate from the lateral interaction of Pt-H bonds. This is in good agreement with the experimental observation that only when the hydrogen adsorption reaches the monolayer can we have a detectable vibrational intensity.[57,58]

Time resolution

Besides its high spectral resolution, Raman spectroscopy can also provide quite high time resolution, which affords additional information about electrochemical interfaces. It is widely accepted that adsorption processes can be divided into two groups: (i) physical adsorption processes are very fast but not easy to monitor the evolution of the spectral change with the potential in a short time period ; (ii) chemical adsorption may in -

volve some very complicated processes such as chemical coadsorption of multicomponents or phase formation, which are possibly very slow to follow the potential change.[54] Therefore it is worthwhile to use time-resolved SERS (TRSERS) to investigate structural dynamic changes of complicated coadsorption processes.

Structural changes of coadsorption with potential

To our knowledge, the dynamic studies including theoretical work on electroadsorption have been based on the assumption that each adsorbate is a rigid body having the same structural dynamics on changing with the potential. However, we have found an interesting phenomenon that is correlated to the structural dynamics of the coadsorbed layer, $i. e.$, different vibration modes of an adsorbate have different response rates to a potential change (potential step).[59]

The time-resolved SERS spectra show that the band intensities of different vibration modes for the adsorbed TU have surprisingly different response rates as the potential was stepped from $- 0.9$ V to $- 0.3$ V.[59] According to this feature one can divide the major SERS bands into two groups, the first group are the CS and SCNN stretching vibrational modes, and the second group are those related to vibrational modes of the amino group and coadsorbed anion. Following the potential step, the intensities of the first group change more than 80% of that of overall change within the first 0.5 s, and then approach a constant value slowly. For the bands of the second group, the intensities change less than 50% of that of overall change in the initial stage of the potential step then decrease within a prolonged time period (more than 5 min). By analyzing the SERS data, we can determine the surface orientation of TU. The CS bond directly binds to the Ag surface, while the protonated amino groups and anion are in the outer part of the adsorbed layer. Therefore, effects of the electric field crossing the double layer may be significantly different on different functional groups of TU. The slow structural change is due to the rearrangement of the amino groups and the coadsorbed ClO_4^- in order to form a compact coadsorbed layer. This example stresses the possibility to focus individually on different groups (or intra-molecular bondings) of the adsorbate in the dynamic studies, particularly on some complicated coadsorption processes.

Potential averaged Raman spectroscopy for time-resolved studies

With the use of ultramicroelectrode as high as sub-microsecond resolution can be obtained.[5] It should be noted that the time resolving value is limited by the detector in the spectroelectrochemical studies.[60] It means that one needs to purchase a costly gatable ICCD for the time-resolved Raman study. Recently a novel technique named as potential averaged Raman spectroscopy (PARS) has been developed in our laboratory. By taking advantage of easily switching electrode potential, the time-resolving value is no longer dependent on the detector but only on the electrochemical experimental parameters.[61] PARS method is based on the application of a continuous waved potential modulation to the electrode during the acquisition period. A PARS spectrum is recorded while the two electrode potentials of interest are being rapidly modulated, and the spectrum contains the comprehensive information of surface species at the two modulated electrode potentials. Later, the each spectrum at individual potential can be extracted by deconvolution. By properly choosing the two modulating potentials and frequencies in sequence, one can obtain a set of time-resolved spectra of surface species at the interested electrode potential. Our PARS study on the adsorption/desorption of pyridine (Py) at an Ag micro-electrode can obtain the time-resolved spectra for Py desorbed at - 1. 4 V with a non-gatable CCD detector,[62] as shown in Fig. 4. It is feasible to use PARS to achieve the electrochemical dynamic information at microsecond scale by applying high modulation frequency and a prolonged acquisition time (*e. g.*, 60 s) for getting a better signal-to-noise ratio.

On the other hand, there is another kind of time-resolved SERS study to acquire the signal of the process occurring at a fixed potential after perturbed by a light or magnetic field.[63,64] For this so called pump and probe technique, the time resolution value is determined by the SERS signal and the response of the detector. The higher the time resolution value is anticipated, the stronger the Raman signal should be. Thus, in the nanosecond resolved Raman study, a molecule with very strong resonance and surface enhanced Raman effect was adopted in order to provide strong enough signal. For example, Birke *et al.*, using gating technique, performed a nanosecond time-resolved Raman study on the photo-
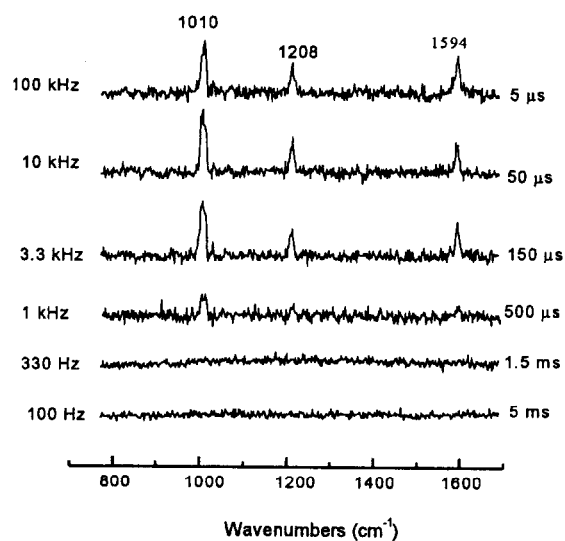
chemical process of flavin.[64]

Fig. 4   Time-resolved SERS spectra of pyridine in 0. 01 mol/L pyridine + 0.1 mol/L KCl at an Ag micro-electrode with diameter of 50 μm when the potential was modulated between two fixed potentials (E_1 = - 0.5 V, E_2 = - 1.4 V) by symmetric square wave. Excitation line: 632.8 nm.

Spatial resolution

It is necessary to note that confocal Raman microscopy is very suitable for the *in-situ* study of electrochemical system. Besides all the features (high horizontal resolution) of a normal Raman microscope it possesses, it also has quite high vertical spatial resolution, which ensures the eliminating of the signal from bulk solution. This is certainly a great help for detecting a relatively weak surface Raman signal from weak SERS or non-SERS active electrodes.

Horizontal resolution

Confocal Raman microscopy can provide quite high horizontal resolution determined by the size of laser spot and the stepping resolution of the X-Y scanning stage. The resolution of *ca*. 1—2 μm is sufficient to study nonuniform surface such as corrosion pit in a REBAR electrode. The corrosion of REBAR (iron-based) in concrete is an important subject. The passive film was

formed by oxidization reduction cycles (ORCs) and the Raman spectra were measured after pitting corrosion had occurred. This kind of study gives us a clear spatial variation of composition and electronic properties of passive film across the pit region on metal electrodes. The Raman spectra in the pit show several corrosion products, including γ-Fe_2O_3, Fe_3O_4, γ-FeOOH and Cl$^-$-containing iron compound.[65]

Surface enhanced Raman imaging (SERI) was first reported by Fujishima et al.[66] With the high spatial resolution, this technique allows for the correlation of the surface structure and Raman behavior. Their primary study focused on the imaging of adsorbates on SERS active Ag surface and the self-assembled monolayer. This technique can certainly be developed into a powerful tool for the investigation of conductive polymer, L-B film, SAM, and the passive film and the microzone corrosion. In the aspect of spatial resolution, it is predicted that, the near field Raman spectroscopy with the spatial resolution up to several nanometer will inevitably emerge in the next few years for studying electrochemical interfaces.[67]

Vertical resolution

It is necessary to note that confocal Raman microscopy is very suitable for the in situ study of electrochemical system. Besides all the features (high horizontal resolution) of a normal Raman microscope, it also has quite high vertical spatial resolution, which ensures the eliminating of the signal from bulk solution. This is certainly a great help for detecting a relatively weak surface Raman signal from weak SERS or non-SERS active electrodes. As a demonstration of its high vertical resolution, the study of solution concentration gradient during electrochemical reactions on an Au electrode by confocal Raman microscopy has been conducted. When a laser spot is focused upon the electrode surface, the Raman signal is mainly contributed by the adsorbed species. However, when the position of the focus is above the surface, the Raman signal mainly comes from the bulk species. Thus by adjusting the focal point at different heights above the electrode surface, one can get a concentration gradient of different solution species based on their spectral signals. It was found in the Raman study of the redox couple $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ that the relative Raman intensity for the two molecules

changes with the distance between the laser focus and the Au electrode surface under controlled potential. At different potentials, the Raman intensity of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ gives the different dependence upon the distance, reflecting the change of the concentration of $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ in the diffusion layer during electrochemical oxidation or reduction process.[65,68]

Another more interesting and important example comes from the electrochemical oxidation process of methanol on a roughened Pt surface in sulfuric acid. During the oxidation process, the focus was moved step by step away from the electrode surface, thus we can see the increase of methanol concentration. Meanwhile the relative intensity of the SO_4^{2-} with respect to HSO_4^- vibrational band increases, which clearly reflects the increase of the solution pH near the electrode surface as a result of methanol oxidation.[69] According to the ratio of the relative intensity of these two species, one is able to estimate the solution pH profile close to the electrode surface during the electrochemical reaction.

Hyphenated technique of Raman spectroscopy with STM

It is necessary to point out that among more than twenty non-electrochemical techniques, including spectroscopies, diffraction techniques and SPM, each technique has its own advantage and disadvantage in probing electrochemical interfaces. For instance, the spatial resolution for Raman spectroscopy only falls into micrometer scale as mentioned above. While scanning tunneling microscopy (STM), which has extremely high spatial resolution up to atomic scale, is making significant contribution to interfacial electrochemistry in the past decade. STM can provide not only explicit topographic information, but also yield new insight into intra/intermolecular electron transfer processes. On the other hand, Raman spectroscopy has been used extensively for structural studies on adsorbates, surface complexes, and thin film modified electrodes. These two techniques are obviously complementary to each other for probing electrochemical interfaces. There is no doubt that much more information can be obtained if one can make use of advantages from these two techniques at the same time to study the electrochemical interface.

We have made a great effort to hyphenate the Ra-

man-STM to carry out the measurements simultaneously. The most serious problem is that the SPM measurement is vitally affected by any mechanical, thermal and electric interference. By taking advantage of the remote operation of the laser optical fiber technique, a Raman-STM hyphenated technique has been set up successfully in our laboratory recently.[70] Fig. 5 is the schematic diagram of the Raman-STM combined base. The remote operation of the optical fiber technique is used so that the simultaneous measurement on one electrochemical cell can be carried out using the two instrument set in two rooms. The STM head was specially designed so that the limited spaces surrounding the STM tip can be fully used for introducing the fibers. Five collection fibers and one excitation fiber were fixed in a fiber fixer of a hemisphere cap through which the fibers can be positioned closely surrounding the STM tip above the sample and close to the tip without any mechanical touch. Furthermore, the graded refractive index lens were fixed at the head of each fiber to ensure larger relative aperture. The scattering light was collected and sent to the next room through five fibers then coupled into the Raman spectrometer. Using an optical multichannel analyzer for recording the Raman signal, the signal acquisition time can be reduced to 0. 1—5 s. Therefore, the laser illumination time can be shortened, thus the thermal interference can be minimized. Simultaneous STM and Raman measurement was made on ORC Ag surface of SCN⁻ adsorption. It was found that STM images are essentially reproducible with a drift of less than 10% before, during and after the Raman measurement.[70] Further tests for the simultaneous STM and Raman measurement were also carried out on the electrodepositon of silver on HOPG electrodes in the presence of thiourea as an organic additive to correlate the SERS activity and surface morphology.[70]

Prospectus of Raman spectroscopy in electrochemical applications

Recently a breakthrough in SERS field was made by Kneipp's group and Nie's group.[71,72] They used crystal violet and R6G respectively to obtain the SERS or SERRS spectra on single Ag particles. The estimated enhancement of the signal amounts to 10^{14}—10^{15}, which is much higher than the widely accepted enhancement of 10^6. The result clearly shows that, different shape and size of the particle could have a very different enhancement effect. Using a filtration method to get Ag particles of different size from the Ag colloidal, Nie et al. found that the Ag particles with size between 80 nm to 100 nm could have the highest enhancement effect. The molecule with very large Raman cross section was used to make it possible to obtain Raman signal from the single molecule.[73] There will be no doubt that by using well controlled surface nanostructuring technique, many electrode substrates with extremely high SERS activity can be made and the detection sensitivity of SERS for variety of electrode materials will be further improved.
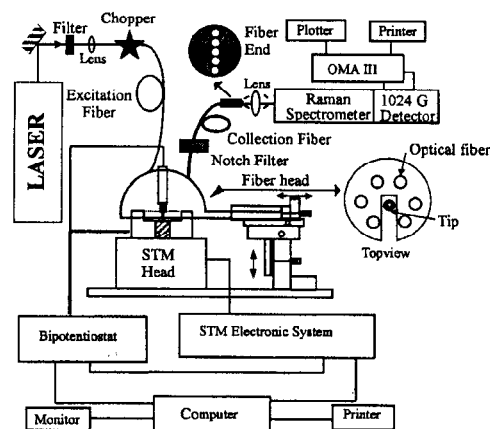

Fig. 5   Schematic diagram of the hyphenated system of laser Raman and STM for electrochemical investigation.

Although there have been some reports on surface Raman study on atomic flat single crystal surfaces, the early studies were restricted to vacuum/solid and air/solid interfaces.[74-77] Only recently, the SERS study on true smooth single crystal surface has been accomplished.[20,78-80] Bryant et al. observed the Raman spectra of thiophene on smooth Pt surfaces.[20] Otto's group, on the other hand, using an ATR Raman cell with Otto configuration obtained Raman signal from different single crystal surfaces of Cu.[78] The enhancement factor for single crystal surface is estimated to be around 1 to 2 orders. Whilst, Futamata using an ATR Raman cell with Kretchmann configuration assisted by the surface plasma enhancement, obtained very weak SERS from Ag(111) surface, as well as Pt surface and Ni surface.[79,80] It should be noted that, at present, only very limited numbers of molecules with large Raman cross section can be used for this difficult investigation.[78-80] Further improvement on the Raman instrumentation to extend this study

to other molecules, which provides comparable case with that of the rough surface, can surely not only provide more insight into the SERS mechanism, but also be very helpful to expand widely the electrochemical applications of Raman spectroscopy.

In summary, we are optimistic that with the improvement of Raman instrument and the development of electrode substrates, both in the detection sensitivity and in the spatial and time resolution, the research capability of Raman spectroscopy will be greatly enhanced, and thus can be developed into a powerful and general tool in electrochemistry.

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References

1. Christensen, P. A. ; Hamnet, A. , *Techniques and Mechanisms in Electrochemistry*, Chapman & Hall, London, 1993.
2. Abruña, H. D. , *Electrochemical Interfaces-Modern Techniques for In-situ Characterization*, VCH, New York, 1991.
3. Gale, R. J. , *Spectroelectrochemistry-Theory and Practice*, Plenum Press, New York, 1988.
4. Itaya, K. , *Prog. Surf. Sci.* , **58**, 121(1998).
5. Andrieux, C. P. ; Hapiot, P. ; Saveant, J. M. , *Chem. Rev.* , **90**, 723(1990).
6. Fleischmann, M. ; Hendra, P. J. ; Mcquillan, A. J. , *Chem. Phys. Lett.* , **26**, 163(1974).
7. Jeanmaire, D. L. ; Van Duyne, R. P. , *J. Electroanal. Chem.* , **84**, 1(1977).
8. Albrecht, M. G. ; Creighton, J. A. , *J. Am. Chem. Soc.* , **99**, 5212(1977).
9. Pettinger, B. , in "*Adsorption of Molecules at metal Electrodes*", Chapter.6, Eds. Lipkowski, J. ; Ross, P. N. , VCH, New York, 1992.
10. Fleischmann, M. ; Hill, I. R. , *Comprehensive Treatise of Electrochemistry*, Ed. White, R. E. ; Bockris, J. O'M. ; Conway, B. E. ; Yeager, E. ,Vol. 8, Plenum, New York, 1985, p.373.
11. Chen, T. T. ; Chang, R. K, *Surf. Sci.* , **158**, 325(1985).
12. Tian, Z. Q. ; Sigalaev, S. K. ; Zou, S. Z. ; Mao, B. W. ; Funtikov, A. M. ; Kazarinov, V. E. , *Electrochim. Acta*, **39**, 2195(1994).
13. Zou, S. Z. ; Chen, Y. X. ; Mao, B. W. ; Tian, Z. Q. , *J. Electroanal. Chem.* , **424**, 19(1997).
14. Chen, Y. X. , *Ph. D. Thesis*, Xiamen University, Xiamen.

15. Chen, Y. X. ; Zou, S. Z. ; Huang, K. Q. ; Tian, Z. Q. , *J. Raman Spectrosc.* , **29**, 749(1998).
16. Fleischmann, M. ; Tian, Z. Q. ; Li, L. J. , *J. Electroanal. Chem.* , **217**, 397(1987).
17. Leung, L. W. H. ; Weaver, M. J. , *J. Am. Chem. Soc.* , **109**, 5113(1987).
18. Bilmes, S. A. ; Rubim, J. C. ; Otto, A. ; Arvia, A. J. , *Chem. Phys. Lett.* , **159**, 89(1989).
19. Fleischmann, M. ; Sockalingum, D. ; Musiani, M. M. , *Spectrochim. Acta A* , **46**, 285(1990).
20. Bryant, M. A. ; Loa, S. L; Pemberton, J. E. , *Langmuir*, **8**, 753(1992).
21. Ren, B. ; Huang, Q. J. ; Cai, W. B. ; Mao, B. W. ; Liu, F. M. ; Tian, Z. Q. , *J. Electroanal. Chem.* , **415**, 175 (1996).
22. Tian, Z. Q. ; Ren, B. ; Chen, Y. X. ; Zou, S. Z. ; Mao, B. W. , *J. Chem. Soc.* , *Faraday Trans.* , **92**, 3829 (1996).
23. Gao, J. S. ; Tian, Z. Q. , *Chem. Phys. Lett.* , **262**, 151 (1996).
24. Tian, Z. Q. ; Ren, B. ; Mao, B. W. , *J. Phys. Chem. B*, **101**, 1338(1997).
25. Huang, Q. J. ; Yao, J. L. ; Mao, B. W. ; Gu, R. A. ; Tian, Z. Q. , *Chem. Phys. Lett.* , **271**, 101(1997).
26. Gu, R. A. ; Yao, J. L. ; Yuan, Y. X. ; Tian, Z. Q. ; Ren, B. , *Chem. J. Chin. Univ.* , **18**, 1680(1997).
27. Gao, J. S. ; Tian, Z. Q. , *Spectrochim. Acta Part A*, **53**, 1595(1997).
28. Li, X. Q. ; Ren, B. ; Tian, Z. Q. , *Chem. J. Chin. Univ.* , **19**, 120(1998).
29. Cai, W. B. ; Ren, B. ; Li, X. Q. ; She, C. X. ; Liu, F. M. ; Cai, X. W. ; Tian, Z. Q. , *Surf. Sci.* , **406**, 9 (1998).
30. Cai, W. B. ; She, C. X. ; Ren, B. ; Yao, J. L. ; Tian, Z. W. ; Tian, Z. Q. , *J. Chem. Soc.* , *Faraday Trans.* , **94**, 3127(1998).
31. Tian, Z. Q. ; Gao, J. S. ; Li, X. Q. ; Ren, B. ; Huang, Q. J. ; Cai, W. B. ; Liu, F. M. ; Mao, B. W. , *J. Raman Spectrosc.* , **29**, 703(1998).
32. Cao, P. G. ; Yao, J. L. ; Ren, B. ; Mao, B. W. ; Gu, R. A. ; Tian, Z. Q. , *Chem. Phys. Lett.* , **316**, 1(2000).
33. Huang, Q. J. ; Li, X. Q. ; Yao, J. L. ; Ren, B. ; Cai, W. B. ; Mao, B. W. ; Tian, Z. Q. , *Surf. Sci.* , **427/428**, 162(1999).
34. Yao, J. L. ; Xu, X. ; Pan, G. P. ; Xie, Y. ; Sun, D. M. ; Xue, K. H. ; Tian, Z. Q. , sumitted to *Chem. Commun.*
35. Ren, B. ; Xu, X. ; Li, X. Q. ; Cai W. B. ; Tian, Z. Q. , *Surf. Sci.* , **427/428**, 157(1999).
36. Bewick, A. ; Pons, S. , in "*Advances in Infrared and Raman Spectroscopy*", Eds. Clark, R. J. H. ; Hester, R. E. , Vol. 12, Wiley, London, 1985.
37. Richmond, G. L. , in "*Electrochemical Interfaces-Modern*

Techniques for In-situ Characterization", Ed. Abruña H. D., VCH, New York, 1991, p. 265.

38. Zou, S. Z.; Williams, C. T.; Chen, E. K. Y.; Weaver, M. J., *J. Am. Chem. Soc.*, **120**, 3811(1998).

39. Zou, S.; Williams, C. T.; Chen, E. K. Y.; Weaver, M. J., *J. Phys. Chem. B*, **102**, 9743(1998).

40. Zou, S.; Weaver, M. J.; Li, X. Q.; Ren B.; Tian, Z. Q., *J. Phys. Chem. B*, **103**, 4218(1999).

41. Martin, F.; Prieto, A. C.; De Saja, J. A.; Aroca, R., *J. Mol. Struct.*, **174**, 363(1988).

42. Xue, G.; Dong, J.; Zhang, M., *Appl. Spectrosc.*, **45**, 756(1991).

43. Xue, G.; Lu, Y.; Zhang, J., *Macromolecules*, **27**, 809 (1994).

44. Xue, G.; Lu, Y.; Shi, G., *Polymer*, **35**, 2448 (1994).

45. Dong, J.; Sheng, Z.; Xue, G., *Chem. Phys. Lett.*, **231**, 183(1994).

46. Dong, J.; Sheng, Z.; Xue, G., *Spectrochim. Acta*, **51A**, 1031(1995).

47. Cao, Q.; Li, F. T.; Lu, Y.; Xue, G., *Spectrosc. Lett.*, **31**, 167(1998).

48. Liu, F. T.; Lu, Y.; Xue, G., *Appl. Spectrosc.*, **51**, 804(1997).

49. Tian, Z. Q.; Lei, L. C.; Jing, X. B., *Acta Phys-Chim. Sin.*, **4**, 458(1988).

50. Zhong, C. J.; Tian, Z. Q.; Tian, Z. W., *Sci. China B*, **12**, 1259(1989).

51. Chen, Y. Z.; Gu, Z. J; Tian, Z. Q., *Acta Phys-Chim. Sin.*, **9**, 277(1993).

52. Ren, B.; Liu, F. M.; Xie, J.; Mao, B. W.; Zu, Y. B.; Tian, Z. Q., *Appl. Phys. Lett.*, **72**, 933(1998).

53. Tian, Z. Q.; Li, W. H.; Qiao, Z. H.; Lin, W. F.; Tian, Z. W., *Russ. J. Electrochem.*, **31**, 1014(1995).

54. Tian, Z. Q., *Acta Phys.-Chim. Sin.*, **4**, 344 (1988).

55. Zhong, Q. L.; Wang, D. Q.; Liu, F. M.; Su, X. Q.; Shi, C. H.; Tian, Z. Q., *Acta Phys-Chim. Sin.*, **14**, 562(1998).

56. Jerkiewicz, G., *Progress Surf. Sci.*, **57**, 137 (1998).

57. Xu, X.; Ren, B.; Wu, D. Y.; Xian, H.; Lu, X.; Shi, P.; Tian, Z. Q., *Surf. Interface analysis*, **28**, 111 (1999).

58. Xu, X.; Wu, D. Y; Ren, B.; Xian, H.; Tian, Z. Q., *Chem. Phys. Lett.*, **311**, 193(1999).

59. Tian, Z. Q.; Li, W. H.; Mao, B. W.; Gao, J. S., *J. Electroanal. Chem.*, **379**, 271(1994).

60. Fleischmann, M.; Graves, P. R.; Robinson, J., *J. Elec-*

troanal. Chem., **182**, 73(1985).

61. Tian, Z. Q.; Li, W. H.; Zou, S. Z.; Gao, J. S., *Appl. Spectrosc.*, **50**, 1569(1996).

62. She, C. X.; Cai, W. B.; Yao, J. L.; Mao, B. W.; Tian, Z. Q., in "*The XVIth International Conference on Raman Spectroscopy*", Ed. Heyns, A. M., John Wiley & Sons Ltd., 1998, p. 422.

63. Shi, C.; Zhang, W.; Lombardi, J. R.; Birke, R. L., *J. Phys. Chem.*, **96**, 10093(1992).

64. Zhang, W.; Vivoni, A.; Lombardi, J. R.; Birke, R. L., *J. Phys. Chem.*, **99**, 12846(1995).

65. Ren, B.; Yao, J. L.; Li, X. Q.; Chen, X. G.; Liu, F. M.; Yang, Y.; Lin, Z. G.; Tian, Z. Q., in "*The XVIth International Conference on Raman Spectroscopy*", Ed. Heyns, A. M., John Wiley & Sons Ltd., 1998, p.808.

66. Yang, X. M.; Tryk, D. A.; Hashimoto, K.; Fujishima, A., *J. Raman Spectrosc.*, **29**, 725(1998).

67. Zhang, S. L., *Chin. J. Light Scattering*, **5**, 50(1993).

68. Ozeki, T.; Irish, D. E., *J. Electroanal. Chem.*, **280**, 451(1990).

69. Ren, B.; Li, X. Q.; She, C. X.; Tian, Z. Q., *Electrochim. Acta*, in press.

70. Tian, Z. Q.; Li, W. H.; Ren, B.; Mao, B. W.; Chen, J. G.; Mu, J. Q.; Zhuo, X. D.; Wang, D., *J. Electroanal. Chem.*, **401**, 247(1996).

71. Nie, S.; Emory, S. R., *Science*, **275**, 1102(1997).

72. Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L. T.; Itzkan, I.; Dasari, R. R.; Feld, M. S., *Phys. Rev. Lett.*, **78**, 1667(1997).

73. Emory, S. R.; Nie, S., *J. Phys. Chem. B*, **102**, 493 (1998).

74. Campion, A.; Mullians, D. R., *Chem. Phys. Lett.*, **94**, 576(1983).

75. Pettenkofer, C.; Otto, A., *J. Phys. (Paris)*, **C10**, 337 (1983).

76. Jiang, X.; Campion, A., *Chem. Phys. Lett.*, **140**, 95 (1987).

77. Kambhampati, P.; Child, C. M.; Foster, M. C.; Campion, A., *J. Chem. Phys.*, **108**, 5013(1998).

78. Bruckbauer, A.; Otto, A., *J. Raman. Spectrosc.*, **29**, 665(1998).

79. Futamata, M, in "*The XVIth International Conference on Raman Spectroscopy*", Ed. Heyns, A. M., John Wiley & Sons Ltd., 1998, p.356.

80. Futamata, M., *Surf. Sci.*, **89**, 386(1997).
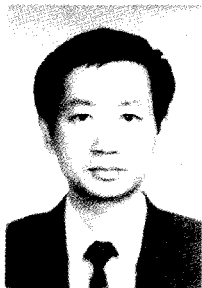
Prof. Zhongqun Tian received his B.S. at Xiamen University in 1982. He entered Department of Chemistry, University of Southampton of United Kingdom in 1983 under supervision of Prof. Martin Fleischmann, and received the Ph.D. in 1987. Since then he has been active in research and teaching at Xiamen University. He was appointed to full professor in 1992. His current research interests are spectroelectrochemistry, surface enhanced Raman spectroscopy (SERS) and nano-electrochemistry. He is the author of 105 articles and a member of editorial boards of six Chinese scientific journals.
(E-mail: zqtian@xmu.edu.cn)
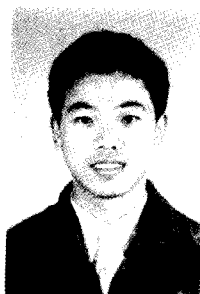
Dr. Bin Ren received his B.S. at Xiamen University in 1992. From 1992 to 1998, he worked for his Ph.D. degree under the supervision of Prof. Zhongqun Tian and Zhaowu Tian, and received his Ph.D. degree in 1998. From 1997 to 1998, he served as a visiting scholar at The City College of New York in profs. D.L. Akins and R.L. Birke's groups. Now he is a research assistant at the Department of Chemistry of Xiamen University. His current research interests are spectroelectrochemistry and scanning probe microscopy.
(E-mail: bren@jingxian.xmu.edu.cn)

(E9908096   ZHOU, X.M.; LING, J.)