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Electrochemically Roughened Rhodium Electrode as a Substrate for Surface-enhanced Raman Spectroscopy

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A method to produce a substrate suitable for surface-enhanced Raman study on the pure massive Rh electrode was developed. The surface-enhanced Raman scattering (SERS) active Rh electrode with good stability, reversibility, and ease of preparation can be obtained by the control-current electrochemical roughening method. The surface enhancement factor was estimated to be 3 orders of magnitude. Such kind of enhancement allows the investigation of not only some molecules of large Raman cross-section (e.g., pyridine) but also other molecules of very small Raman cross-section (like CO). This result shows that the Rh surface can be used as a useful substrate for the combined electrochemical and Raman study of some systems that are both of fundamental and application interest.

1. Introduction

Raman spectroscopy is a powerful technique that can provide structural information at the molecular level.[1] However, only after the discovery of surface-enhanced Raman scattering (SERS) effect has it become one of the most widely used techniques in physical chemistry and surface sciences.[2−4] That only Ag, Au, and Cu can produce prominent SERS signal of practical significance greatly limits the application of this technique. Recently, our group has made some progresses in extending SERS to pure transition metal surfaces, such as Pt, Ni, Fe, Co, etc.[5−9] Rh is one of the most important materials in surface sciences because it has been widely used as catalyst or cocatalyst in the catalytic or electrochemical reactions.[10,11] For example, it has been used as the catalysts for the decomposition of NO,[12] oxidation of CO,[13] and reduction of CO_2,[14] which are of close concern with the environmental problems in the world. It will be of great help in understanding the interfacial phenomena at the molecular level and possibly the complex SERS mechanisms if we can extend SERS study to the Rh surface. However, how to get a stable and high SERS active Rh surface is a key problem. It has been found that Rh is very difficult to be roughened because it will grow naturally in air an oxide layer to prevent the further oxidation of the surface.[15] Furthermore, Rh can be easily oxidized to various types of rhodium oxide, which can be seen from the phase diagram of Rh.[16] A method using fast electrochemical cyclic voltammetric technique was proposed to obtain a SERS-active surface.[17] However, when we were trying to repeat their experiment, we found this kind of surface can be damaged easily by the focused laser. It indicates that the surface is not stable enough for surface Raman study, especially microscopic Raman study. Weaver et al. reported the "pinhole-free" method to obtain an Rh film over a SERS-active Au substrate and obtained good SERS signal from such film.[18,19] However, this kind of surface may encounter a stability problem under a severe electrochemical reaction

condition. In an early report of Campion et al., 4-cyanopyridine, a molecule with very large Raman cross section, was used to study the unenhanced Raman scattering.[20] However, the signal-to-noise ratio of the spectra is too low to be used effectively to study the surface processes on the Rh surface, which is reflected by no continuous work on this aspect. In this letter, we report a method that is capable of producing a SERS-active Rh surface with good stability, reversibility, and high SERS activity, which enables the SERS study of Rh surface in various molecular systems.

2. Experimental Section

Raman measurements were conducted on a confocal microprobe Raman system (LabRam I, Dilor). The excitation line is 632.8 nm for a He−Ne laser. It is of single spectrograph setup and uses holographic notch filters to reject the Rayleigh scattering light and the high detection efficiency CCD as the detectors. The confocal depth can be controlled by adjusting the pinhole size. A long-working length (8 mm) microscopic objective of 50 magnification is used in the present study. The intensity and frequency are calibrated based on a Si (111) wafer.

The potential was controlled by a PAR 173 potentiostat (EG&G) during the electrochemical roughening and Raman measurements. However, the cyclic voltammograms were recorded on a CHI 631A electrochemical workstation (CH Instruments). The square wave function was generated by a GFG-8016G function generator (Good Will Instrument, Co. Ltd.).

The working electrode was prepared from a polycrystalline Rh rod of 99.9% purity. The rod was first melted by hydrogen−oxygen flame into a bead for a certain time to concentrate the impurities on the surface. Then, the bead was dipped into aqua regia to dissolve impurities followed by cleansing with Milli-Q water. After several cycles of melting and dissolution, the bead was sealed into a Teflon shroud while heating and polished into a mirror finish. The geometric area of the surface is about 0.03 cm^2. A large platinum ring served as the counter electrode. The

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reference electrode was a saturated calomel electrode (SCE); thus, all of the potentials in this work were quoted versus SCE. All of the chemicals are analytical reagents, and the solutions were prepared using Milli-Q water.

3. Results and Discussion

Although a compact oxide film can easily form on the Rh surface, the Rh surface can be roughened by fast electrochemical potential cycling.[17] The surface still looks bright even after roughening but has high SERS activity. However, after being illuminated by a focused laser, the smooth surface was damaged quickly showing a black spot in the illuminating area. Meanwhile, the SERS activity decreased dramatically. Thus, it is necessary to find a method that is capable of producing an electrode surface of good stability.

In the previous SERS study of our group, we found that Pt electrodes can be effectively roughened by a control-potential roughening method.[5] However, this method is invalid for the Rh surface because an initially formed compact oxide layer prevents the further oxidation of the surface. Therefore, developing a new method that enables the roughening of the Rh surface is vitally important. An early work of Shibata indicates that the Rh electrode can be corroded by applying a pulse current with an appropriate frequency; however, no detailed description of the current density and the frequency of the roughening wave function was given, and the only purpose of that report was to obtain a rhodized Rhodium surface for the electrocatalytic study.[21] As is well-known, based on the basic principle of electrochemistry, with a high current density, one can readily polarize a electrode to a high potential, which makes an intensive oxidation of the Rh surface possible. A fast pulse between anodic and cathodic current facilitates a fast place exchange of the surface oxygen with the bulk Rh atoms because of the change of the surface charge. After the systematic work of our group by changing the cathodic and anodic current density and the frequency, we found that an Rh electrode with reasonably good SERS activity could be obtained by the following method in 0.5 M H_2SO_4: First, the smooth Rh electrode was electrochemically cleaned by potential cycling between -0.25 to $+0.8$ V at a rate of 0.5 V s^{-1}; next, a pulsed current with the cathodic and anodic current densities of -950 and $+1600$ mA cm^{-2} and a frequency in the range of 200 to 800 Hz was applied to the electrode for a desired time (a typical time is ca. 2 min); afterward, the electrode was reduced at -0.2 V; and finally, it was stabilized by potential cycling using the same condition as the first step. The roughened Rh surface presents a very uniform surface structure, taking on a color from gray to dark purple. Figure 1 gives the cyclic voltammograms of the Rh surfaces after being roughened for different times. Obviously, a longer roughening time gives a surface of bigger real surface area. It can be clearly seen that all of the cyclic voltammograms present the adsorption and evolution of oxygen on the Rh surface at positive potentials, the hydrogen adsorption/desorption at negative potentials, and the hydrogen evolution at very negative potentials. It means that the roughened Rh surfaces still retain the characteristic electrochemical behavior of the normal Rh surface. This ensures the Raman spectra obtained is representative of that from bulk electrodes, unlike that in the case of Ag, Cu, and Au surfaces, on which the electrochemical behavior changes dramatically after being roughened. Furthermore, because hydrogen adsorption on Rh surfaces is of monolayer amount, the charge of which can be used as a criterion to estimate the real surface area of the roughened Rh electrode. It is known that the charge (Q_S) for
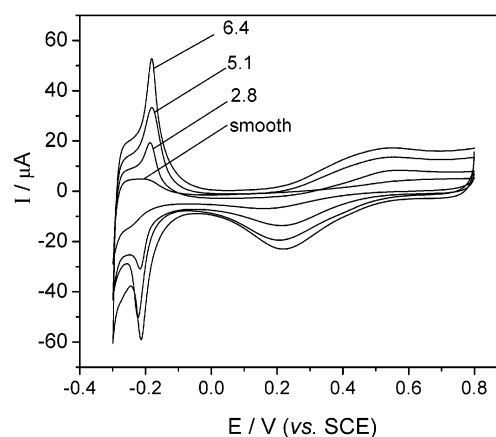
Figure 1. Cyclic voltammograms of roughened Rh electrodes with different roughness factors in 0.1 M H_2SO_4 solution. Scan rate: 50 mV s^{-1}.
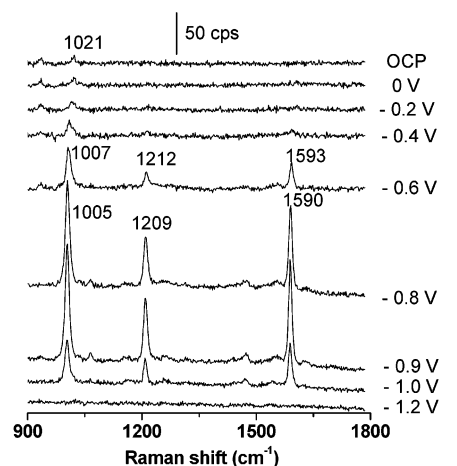
Figure 2. Surface-enhanced Raman spectra of pyridine adsorbed on a roughened Rh surface in 0.1 M NaClO$_4$ + 0.01 M pyridine solution. Excitation line: 632.8 nm. Acquisition time: 20 s.

the formation of a full monolayer adsorbed hydrogen on a ideally smooth polycrystalline Rh surface is about 240 μC cm^{-2},[22] and the increase in the real surface area of the Rh electrode after being roughened can be calculated by $R = Q_R/Q_S$, where Q_R is the charge of hydrogen monolayer adsorption on the rough Rh surface. The R value is important to estimate the possible surface enhancement effect and was denoted as the roughness factor in the present study, and it is in the range of $4-15$ depending on roughening time.

To check the SERS activity of this kind of surface, we selected pyridine as the probe molecule. The solution used was 0.01 mol L^{-1} pyridine + 0.1 mol L^{-1} NaClO$_4$. It could be seen from Figure 2 that the surface Raman signal of pyridine is very strong, with characteristic bands appearing at 1005, 1208, and 1590 cm^{-1}.[23] The relative band intensity and the band position are very similar to that of the Pt electrode however distinctively different from that of noble metals (Ag, Au, and Cu) and iron group metals (Fe, Co, and Ni).[6−8] This reflects the distinct different interactions of pyridine with different transition metal surfaces.[23] Furthermore, the signal obtained from the roughened surface is apparently better than that from rhodium colloids.[24]

It should be noted that the roughened surface shows such a good stability that even after a long time exposure in air it can still be used for Raman study only after a cleaning in sulfuric solution. To investigate the reversibility of the surface, a very negative or positive potential was applied to the electrode first, and then the potential was set at -0.8 V. It was found that the
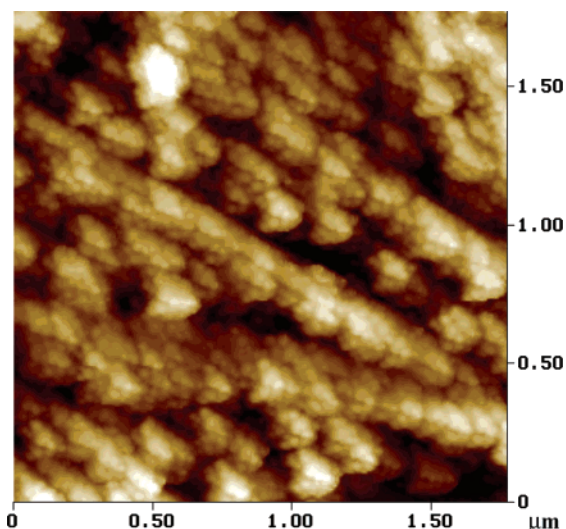
Letters

J. Phys. Chem. B, Vol. 107, No. 4, 2003 **901**

Figure 3. AFM image of a roughened Rh electrode. The image was obtained in tapping mode.

Figure 4. Surface-enhanced Raman spectra of a roughened Rh surface in 0.1 M CH_3OH + 0.1 M $NaSO_4$. 0.2 M methanol was added into a Raman cell containing 0.2 M Na_2SO_4 solution with the electrode controlled at −0.6 V to form the final measuring solution.

pyridine signal reduced by about 20% and 50% of the freshly prepared Rh surface. One might think that the reversibility of this electrode is not as good as that of the Pt surface on which the surface Raman signal can be fully recovered. However, if the electrode was cleaned in 0.1 M H_2SO_4 solution until reproducible cyclic voltammograms were obtained, the pyridine signal can be recovered to about 80% of the freshly prepared Rh surface. Further treatment on this kind of electrode will not lead to an obvious change of the SERS activity. This gives us an indication that, the SERS active site did not decompose at very negative and positive potential. The reason for the decrease in the SERS intensity is due to a certain kind of reaction on the surface, the product of which will block the surface sites. After considering this factor, the Rh surface still presents very good stability and reversibility that are very important for it to be a SERS substrate for general purpose.

With the surface roughness factor (R) obtained by the method mentioned above and the surface and solution Raman spectra of adsorbed and free pyridine, we can estimate the surface enhancement factor for pyridine adsorbed on Rh to be about 4000, according to the method proposed in ref 25. However, because the roughening current and roughening time will also affect the real surface area of Rh, the surface enhancement factor will be slightly different for different surfaces.

It is very natural that one may wonder which kind of surface can give surface enhancement. The Rh electrode after being roughened presents a very uniform surface and carpet-like structure in a video monitor equipped with the Raman microscopy; however, it is impossible to see the structure at the micron or submicron scale. To know in more detail the morphology of the roughened Rh surface, an AFM measurement was done. Figure 3 gives the AFM image of the roughened Rh surface. In accordance with the observation by video camera, the AFM image presents morphology of a very uniform surface, with aggregates in the dimension of 100 nm. On these aggregates, there is some small particles in the range of 20−40 nm. At present we do not have a definite answer to which kind of structure (corrugation or particle) contributes to the enhancement of the surface Raman signal. It is likely that the particles with the size of 20 to 40 nm should play a key role. It is very important that one should prepare a substrate with ordered structure of controlled size in order to get the answer. This work is now underway in our lab by using the template method.
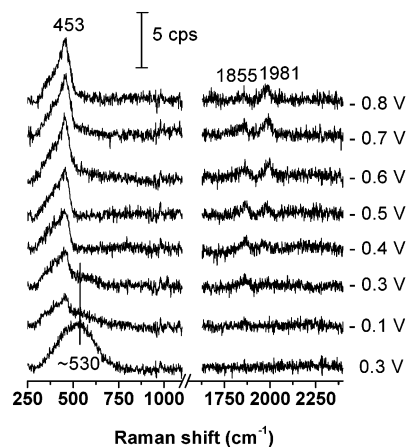
That the Raman signal with very good signal-to-noise ratio can be obtained from pyridine encourages us to investigate systems of very small Raman cross section. One of such systems is the electrocatalytic oxidation of methanol on the Rh surface.[26,27] Two bands can be observed with comparable intensity in the high frequency region, see Figure 4. This result is in good agreement with that of IR studies, in which the two bands were assigned to the bridge-bonded CO and linearly bonded CO, respectively.[28,29] However, only one broad band could be detected in the low-frequency region, which is different from that obtained from Pt surfaces.[30] It is possible that the Rh−C−Rh band has a very close frequency to that of the Rh−C band. Therefore, the two bands overlap with each other. This is evidenced by the asymmetric shape of the 453 cm^{-1} band. The ability to detect the vibrational information reflecting the bonding of the surface species with the substrate demonstrates the advantage of Raman spectroscopy. When the electrode potential is more positive than −0.5 V, the oxidation of the adsorbed CO on the surface is evidenced by the decrease in the band intensities of all of the bands related to CO. At 0.3 V, the signal from adsorbed CO disappeared totally, instead a strong and broad band at around 530 cm^{-1} was observed. It is the characteristic band of Rh oxide. The success of this study indicates that we may further be able to use such a surface to investigate the well-studied bi-metallic catalyst system,[31] by which we can understand not only the dissociation process of methanol on Pt and Rh surfaces but also the role of Rh in the oxidation of CO and methanol.

Summary

In this letter, we proposed a method that is capable of producing a rhodium surface with reasonably high SERS activity. Both SERS and electrochemical studies show that the roughened Rh surface presents very good stability, reversibility, and the characteristic electrochemical properties of the smooth surface. The high SERS activity of the Rh electrode enables the SERS study of pyridine and CO, a dissociative product of methanol. This study demonstrates the applicability of using Rh as a ubiquitous SERS substrate for investigating systems of both fundamental and application interest. Using this surface, we can further investigate some more interesting systems, such as the hydrogen adsorption, CO_2 reduction and the oxidation of small organic molecules, etc. The work along this avenue is now underway in our lab.

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