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Rhodium as a Ubiquitous Substrate for Surface Enhanced Raman Spectroscopy

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Detailed abstract: Raman Spectroscopy is a powerful technique in characterizing the molecular structure at the molecular level. However, only after the discovery of surface enhanced Raman scattering (SERS) effect, has it become one of the most widely used technique in surface sciences. The limitation that only Ag, Au and Cu can produce prominent SERS signal of practical significance, greatly hinders the application of this technique. Recently our group has made great progress in extending SERS to pure transition metal surfaces, such as Pt, Ni, Fe, Co etc^[1]. Rh, due to its special application as catalysts in the catalytic or electrochemical reaction has made it one of the most important materials in surface sciences. It will be of great help for understanding the interfacial phenomenon and possibly the SERS mechanisms if we can extend SERS to the Rh surface. However, It has been found that, Rh is very difficult to be roughened since it will grow naturally in air an oxide layer which will retard the further formation of surface oxides. Furthermore, Rh is very easily oxidized to various forms of rhodium oxides as can be found from the phase diagram of Rh^[2]. How to select a method to roughen the surface and to extend SERS to Rh seems not an easy task.

In our previous study, we found that Rh could not be successfully roughened using controlled-potential roughening procedure as has been used for Pt. In the present study we developed a method to roughen the Rh surface for obtaining strong Raman scattering based on the work of Shibata^[3]. It reveals that the etching of Rh is possible by applying a pulse current with a suitable

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frequency. With the pulse current, we can easily polarize the electrode to a high potential with a high current density, that makes the deep oxidation of Rh surface possible. After the systematic work of our group, we found that an Rh electrode with reasonable good SERS activity could be obtained by applying the current between -30 mA to +50 mA with a frequency ranging between 200 to 800 Hz. The roughened Rh surface presents a quite uniform surface structure. The most important feature is the electrochemical behavior of this kind of electrode is almost the same as that of the smooth surface, see Fig. 1. It can be clearly seen that both cyclic voltammograms present the oxidation of Rh at positive potentials and the hydrogen adsorption/desorption at negative potentials, and at very negative potentials, the hydrogen evolution occurs on the surface. This ensures the Raman spectra obtained is in representative of that from bulk electrodes, which is distinctly different from Ag, Cu and Au surfaces that after roughened in KCl solution, the electrochemical behavior changed dramatically.

Using this kind of surface, we selected pyridine as the model molecule to check the applicability of this method for the surface Raman study. The Raman spectra were acquired on a LabRam I spectrometer that has very high detection sensitivity. The solution used was 0.01 mol/L pyridine + 0.1 mol/L NaClO₄. It could be seen from Fig. 2 that the surface Raman signal of pyridine is very strong, with characteristic bands appearing at 1 003, 1 208 and 1 590 cm⁻¹ respectively. The relative band intensity and the band position is very close to that of Pt electrode while distinctively different from that of noble metal and Fe and Ni electrodes. This indicates a different interaction of pyridine with different transition metal surfaces.

This kind of surface shows quite good stability. It is very stable even after a long time exposure in air. Upon very negative or positive potential excursion of the electrode then back to -0.8 V, the pyridine signal reduced to about 20% and 50% that of the freshly prepared Rh surface.

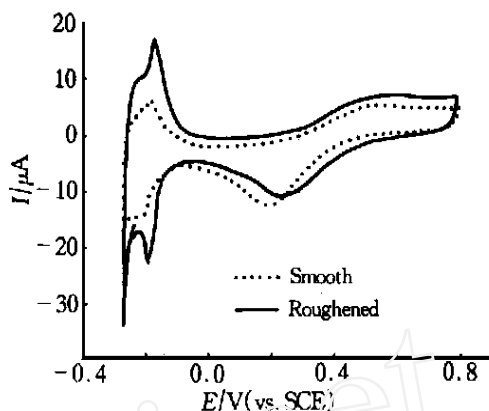


Fig. 1 Cyclic Voltammograms of the smooth and roughened Rh in 0.5 mol/L H₂SO₄

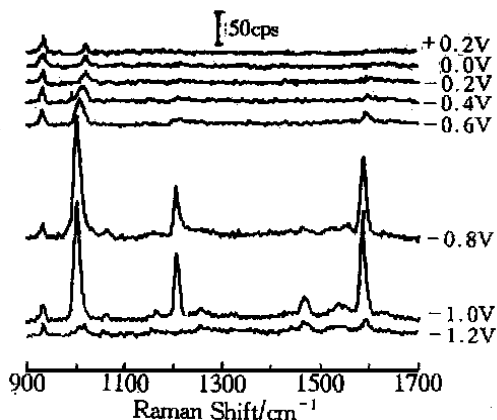


Fig. 2 SERS spectra of roughened Rh in 0.1 mol/L NaClO₄ + 0.01 mol/L Pyridine

One might think that the reversibility of this electrode is not as good as that of the Pt surface. However, before or after each experiment, when it was cleaned in 0.1 mol/L H_2SO_4 solution until reproducible cyclic voltammograms obtained, the pyridine signal can be recovered to about 80% compared with that of the freshly prepared Rh surface, then will not change with the further treatment. This gives us an indication that, the SERS active site did not decompose during the negative and positive potential excursion, instead it is very possible that a certain kind of reaction occurs on the surface, thus the surface sites are blocked by the product. In this aspect, the Rh surface still presents quite good stability and reversibility which is very important for it to be a ubiquitous SERS substrate.

After obtaining the surface roughness factor from the cyclic voltammogram of Rh in sulfuric acid solution, and the surface and solution Raman signal of pyridine, we estimated the surface enhancement factor for pyridine adsorbed on Rh is about 4 000. The obtaining of the Raman signal with very good signal to noise ratio encourage us to investigate a system of wide interest in the fuel cell and electrocatalytic system—CO adsorption on the Rh surface, where very small Raman cross section has been estimated for CO. Similar to that obtained from IR study, a band at about $2\ 021\ \text{cm}^{-1}$ could be detected with the concurrent appearance of a band at $452\ \text{cm}^{-1}$. These two bands could be ascribed to the stretching vibration of CO and Rh-C of the linearly adsorbed CO. The great advantage of this method compared with IR lies in its capability of detecting the vibrational information reflecting the interaction of the surface species with the substrate. Furthermore, we could also observe a weak band at $1\ 900\ \text{cm}^{-1}$ related to the bridge-bond CO on Rh, which is much stronger than that obtained from Pt surface. At relatively positive potential a band at *ca.* $500\ \text{cm}^{-1}$ could be detected, possibly from the Rh oxide when the CO is still existing on the surface. This information may provide some evidence for the surface reaction mechanism of CO on Rh.

This study clearly demonstrates the applicability of using Rh as a ubiquitous SERS substrate for investigating systems of both fundamental and applicable interest. This will further allows the investigation of some more interesting systems, such as the hydrogen adsorption, CO_2 reduction and methanol oxidation. The work along this avenue is now undergoing in our lab.

Key words: Surface enhanced Raman Spectroscopy, Rhodium, Roushened, Carbon monoxide, Pyridine

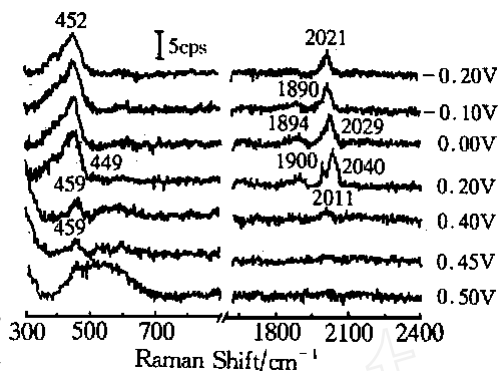


Fig. 3 SERS spectra of CO adsorbed on a roughened Rh in 0.1 mol/L H_2SO_4

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铑电极上的表面增强拉曼光谱研究

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摘要: 本文简要介绍了将铑电极用于表面增强拉曼光谱(SERS)研究的方法. 具有较强活性的铑电极可以通过对电极施加方波电流进行恒电流粗糙获得. 对模型分子吡啶进行的表面拉曼光谱研究表明,该电极具有很好的稳定性和可逆性,并且其表面增强因子可达 4000. 在对铑电极上一氧化碳的氧化过程进行的拉曼光谱研究中同时检测到桥式和线型吸附的 C-O 和 Pt-C 振动的拉曼信号. 本研究表明铑电极可作为多用的 SERS 基底,拉曼光谱可作为界面研究的通用工具.

关键词: 表面增强拉曼光谱;铑;粗糙;一氧化碳;吡啶