

# 各种过渡金属、合金和半导体电极上的表面拉曼光谱

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## Surface Raman Spectroscopy of Transition Metal, Alloy and Semiconductor Electrodes

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In the past two decades, only a few metals, mainly roughened Ag, Au and Cu, providing great enhancement ( $10^6$ ) have been applied to study structure and dynamics of molecules adsorbed on surfaces. Due to this serious restriction, Raman spectroscopy has not been used as widely as IR spectroscopy in surface science and electrochemistry. However, people have never given up their efforts to extend Raman spectroscopy to the study of other metallic and non-metallic surfaces. With the aid of the long-range effect of the electromagnetic (EM) enhancement created by the SERS active substrate underneath, weak SERS spectra of adsorbates on transition metal films have been obtained<sup>[1,2]</sup>. But the strong electromagnetic field generated on the SERS active substrate is damped significantly by the coated film so that an ultrathin film has to be deposited with a thickness of only a few atomic monolayers. In consequence, a small portion of residual substrate sites are usually exposed and it is difficult to eliminate entirely the possibility that the adsorbate is bounded to the exposed substrate rather than to the overlayer exclusively. The difficulty in the film preparation and the instability of the film during prolonged measurements also restrict the widespread use of such ultrathin film electrodes. The most fundamental and most difficult approach is to observe surface Raman Scattering directly from bare transition metal surfaces. Some normal or resonance Raman signals from organic molecules on Pt electrodes have been report-

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ed. Although adsorbates with large Raman cross sections were chosen in these studies, the surface Raman signal was barely detectable and it was impossible to investigate the spectra as a function of electrode potential, which is essential for Raman spectroscopy as a general tool in practical applications.

Very recently, the severe limitation encountered in surface Raman investigations appears to be overcome partially by the latest advances in Raman instrumentation with the advent of the CCD camera, the confocal microscope and the holographic notch filter. Our goal is to take advantage of these developments together with different surface roughening procedures to produce high-quality spectra at submonolayer coverage on a variety of metal substrates. Good-quality surface Raman spectra of pyridine adsorbed at Pt, Ni, Ru, Rh, Pd, Co, Fe, Pt/Ir and Si electrodes over a very wide electrode potential region (e. g. - 1.0V to + 1.4V) have been obtained for the first time in our laboratory. The electrodes were either pure metal, alloy and semiconductor materials or thick metal films (with thickness of more than 100 $\mu$  m) electrodeposited on inert glassy carbon (GC) substrates. The SERS spectra are distinctively dependent on nature of the substrate. It is now possible to carry out detailed molecular-level investigation on diverse adsorbates (e. g. pyridine, pyrazine, methanol, ethanol, CO, SCN<sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, H) at various substrates by Raman spectroscopy<sup>[3]</sup>.

We have examined various surface roughening procedures including chemical etching, ex-situ and/or in-situ ORC for different transition metals to obtain surface spectra with better S/N. In order to establish and appropriate surface roughening procedure, various roughening conditions are assessed in terms of the corresponding surface Raman intensity, surface enhancement factor (G) and surface homogeneity. For example, for adsorbed pyridine on roughened Pt surfaces, the G is calculated based on the confocal microscopic feature, showing one to two orders of amplification of Raman signal. With a highly sensitive Raman instrument it seems to be possible to study the diverse metals having very weak enhancement, helping us to judge the contribution of different mechanisms to G.

So far most *in situ* vibrational spectroscopic studies have been focused on vibrational frequency shifts of adsorbate internal modes rather than adsorbate-metal surface modes due to the experimental difficulty of studying low frequency modes, particularly below 400 cm<sup>-1</sup>, for IR spectroscopy and sum frequency generation (SFG). It is of importance to pay special attention to the vibrational bands in the low frequency region in order to gain insight into the nature of the metal-adsorbate bonding. We have studied a methanol/Pt system in

perchloric acid medium and obtained clear evidence that CO, as the poisoning intermediate of the dissociative adsorption product of methanol, is adsorbed at Pt in a negative potential region. The preliminary results demonstrate the virtues of surface Raman spectroscopy for yielding information on surface bonding related to the surface coverage, coadsorbate, and electrode potential.

Due to low Raman cross section of Si-H, especially in conducting Raman experiment *in-situ*, to our knowledge, there was only one *ex-situ* Raman study on detecting the Si-H. Here we report the first *in-situ* Raman study to obtain the surface bonding information during Si etching processes. The result shows Raman spectroscopy can be also used to *in situ* characterize semiconductor surfaces without aid of SERS effect.

*In situ* Raman spectroscopy exhibits several other advantages over IR spectroscopy and SFG for studying solid-liquid interfaces (i) easy use of near-UV, visible, or near-IR light sources for the excitation of the Raman process, (ii) transparency of the electrolyte for the light beam, (iii) application of standard electrochemical cells without the need of using thin liquid cells, and hence, (iv) easy combination with electrochemical transient measurement in faradaic and nonfaradaic regions. However, as mentioned above, the severe obstacle of the lack of detection sensitivity had impeded the wide application of Raman spectroscopy in surface science and electrochemistry. The progress reported in this article provides a good reason to be optimistic that surface Raman spectroscopy will be used as a general technique widely used in surface science and electrochemistry.

自从发现 SERS 以后,人们利用其高灵敏度的特点,在研究电化学界面结构和过程以及吸附态的行为方面作出了贡献,不足之处是二十余年来研究的电极材料一般只限于具有高 SERS 活性的银、金、铜金属,在更具有吸引力的过渡金属上却无法胜任,早期拉曼光与同样的作为分子光谱的 IR、SFG 相比较,由于信噪比小实用价值明显降低,八十年代后期人们尝试在具有强 SERS 活性的银、金表面用电化学方法覆盖一薄层的过渡金属,利用 SERS 电磁场机理 (EM) 的长程效应,取得了某些吸附物种在这些过渡金属上的拉曼光谱信息,如  $\text{CN}^-$  在 Ni-Co-Cu-Zn/Ag<sup>[1]</sup>, CO 在 Pt-Pd/Au<sup>[2]</sup>. 这种方法提供了一条扩展 SERS 于过渡金属电极上的应用途径,不能不说是一种成功,但是人们亦看到 EM 的作用距离是极其有限的,因此过渡金属必须是极薄层(一般为 1 至 5 个单原子层),其覆盖又无法保证均匀铺开,于是可能出现研究的吸附质不是在过渡金属上,而是在尚未被覆盖的基底金属甚至二者的联接边界上,易导致对谱图的错误分析。

过渡金属电极在电化学中具有最重要的实用价值,例如燃料电池中作为燃料的分子氢、低碳含氧化合物或烃类一般都是在铂族元素阳极上实行氧化作用,许多有机电合成化

学往往是在特定的过渡金属电极上完成的,因此认识过渡金属界面层的结构以及吸附的谱学知识,有助于电极反应历程的建立与控制。本实验室继承早期在金、银上附载极薄层过渡金属,从而进行拉曼光谱测试的工作基础,近期采用多种表面粗糙方式和高灵敏度的共焦显微拉曼系统(Lab Raml 型, Dilor),首次在一些过渡金属及其合金和硅电极表面直接测出高质量的拉曼谱,选用的过渡金属有 Pt Pd Rd Ru Rh Ni Co和 Fe等,吸附质包括有较大拉曼散射截面的吡啶,亦有较小截面的 CO 和  $\text{SCN}^-$ ,此外还有吡嗪、二巯基嘧啶、低含碳化合物和卤素等无机阴离子<sup>[3]</sup>,以下作一简要介绍:

**吡啶(Py)和吡嗪(Pz)吸附** 图 1列出一些过渡金属、合金和 Si上吸附 Py的拉曼谱图,对于不同基底其谱峰强度、相对强度、频率均有明显的差异,谱峰随电位变化的情况及其出现的电位区间亦不同,可以比较系统和详细地研究不同金属与 Py相互作用的强弱与作用方式都有不同程度的变化和金属的结构特征。吡嗪的质子碱性吡啶强,分子具有对称中心,属于  $D_{2h}$ 点群,按不相容原理,24个简正振动中全部 g类振动为拉曼活性,除  $A_u$ 外全部 u类振动为红外活性,吡嗪吸附在 Ni电极上的的电位变化谱图的主要特点是一些拉曼禁阻的谱带出现,还发现在信号最强的电位区间(-1.0~ -1.2V)有明显的  $262\text{cm}^{-1}$ 谱峰,可以认为是  $\text{Ni-N}$  伸缩振动模式,由于 Ni与 Pz间的强相互作用结果,导致吸附模式上对称性下降,从  $D_{2h}$ 转变为  $C_{2v}$ 。

**低碳含氧化合物的吸附** 我们从酸性溶液中甲醇在 Pt电极上拉曼谱图,在并不很正的电位区是可以发现  $2050\text{cm}^{-1}$ 左右 CO线性吸附振动外,还伴随  $490\text{--}498\text{cm}^{-1}$ 的 Pt-C伸缩振动峰,随着电位正移两个谱峰同时消失,目前一般接受醇类在电极上的氧化过程是一个复杂的多元步骤,CO这个最简单的低碳含氧化合物只是一个反应中间物,它的强吸附性能往往占据金属表面活性位而不易脱附,电位正移后通过金属表面晶格氧使之转化为  $\text{CO}_2$ 而解吸,但是醇类氧化的首发步骤是脱氢,包括羟基氢和  $\alpha$ 碳氢,如果有足够保留时间,应该在负电位区的谱图上有所反映,我们将结合其它技术继续探讨可能有助于诸多的反应中间体的解释。

**$\text{SCN}^-$ 的吸附**  $\text{SCN}^-$ 无机阴离子的 S端都有孤立电子对,都能与金属的合适空 d轨道配位成键,电位较负时(-1.2~ -1.3V)  $\text{SCN}^-$ 在 Pt电极上主要是以 N端与金属表面接触( $V_{\text{Pt-SCN}} 2073\text{--}2110\text{cm}^{-1}$ ,  $V_{\text{Pt-N}} 354\text{cm}^{-1}$ )。电位较正时(0.4~ 1.2V)  $\text{SCN}^-$ 主要以 S端接触表面( $V_{\text{Pt-SCN}} 211\text{--}2188\text{cm}^{-1}$ ,  $V_{\text{Pt-S}} 281\text{cm}^{-1}$ );在两者的中间电位区间出现两者定位方式并存的现象,随着  $\text{SCN}^-$ 浓度变化,吸附取向转换的电位区间亦相应随着变化。

**氢吸附** 我们首次观察到不同电位时氢吸附在铂电极上的拉曼谱,具有重要作用的氢超电势基本问题,一直只停留在唯象的概念上,如果能在不同电极上对 M-H的键合形式进行深入研究,可能有助于对这个古老的现象在微观的尺度上作出一些新的解释。在 HF刻蚀溶液中,半导体硅表面经电化学处理后,随后经激光照射,在光照进行过程的谱图表明逐渐形成氢化表面。

**经验和体会** 仪器的高检测灵敏度和电极表面的粗糙化处理是成功地开展此工作的关键:共焦显微拉曼仪由于采用 Notch filter和 CCD检测器,检测表面信号的灵敏高于常规仪器约两个数量级。测试使用长焦距(8mm)的 50倍显微物镜头,使得镜头不浸泡在溶液中;测试主要采用仪器内置的 Ne-He激光,到达样品功率约  $12\text{mW}$ ,但功率密度高;电

极表面粗糙可根据体系采用不同方式,如化学刻蚀、电化学沉积、非现场或现场 ORC 等方法,电极经电化学检测其表面状态是稳定的。由于常规 IR 和 SFG 的测定下限一般只在  $600\text{cm}^{-1}$  左右,一般仅能获得吸附质分子内的振动信息,对于研究其频率落在低频范围的吸附质-金属配键(特别是质量较大金属)的振动模式而无法胜任,这是拉曼谱仪需充分发挥的优势。在不远的将来,各类有特色的激光拉曼光谱仪将很有可能从性能和价格等方面与红外光谱仪开展激烈竞争,毫无疑问,拉曼光谱技术将更加普及,在表面、材料、生命和环境科学以及工业的广泛应用中发挥更重要的作用。

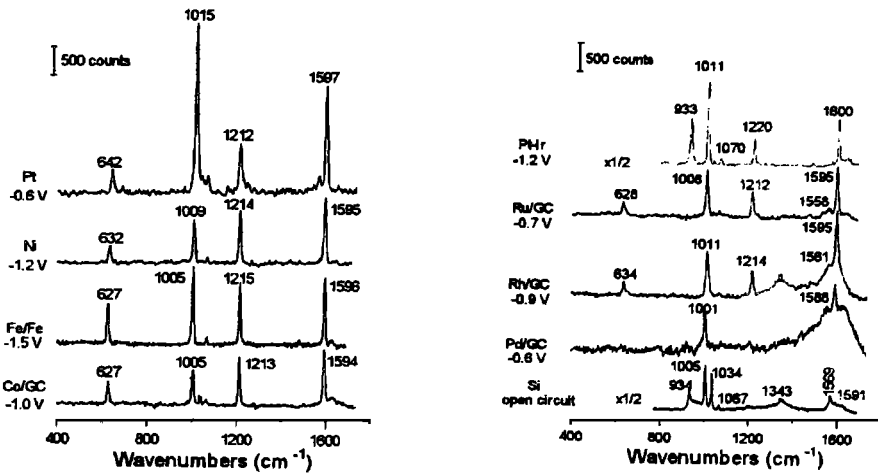


Fig. 1 Surface Raman spectra for pyridine adsorbed on different transition metal, alloy and semiconductor surfaces at the optimized potential.

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