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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（理学） 氏名 ヤン シュオ

学 位 論 文 題 名

Electronic Structure of CO/Pt Electrochemical Interfaces Investigated by Potential Dependent Double
Resonance Sum Frequency Generation Spectroscopy
(電位依存二重共鳴和周波発生分光法による CO/Pt 電極界面の電子構造解析)

Many important catalytic processes take place at solid/liquid interfaces. A detailed understanding of in situ, real time information at solid/liquid interfaces, including geometric structure of the solid surface, electronic structure of the solid/liquid interface as well as molecular structure of reactant, product, intermediate, and solvent at the interface, is essential to clarify the mechanism and improve the efficiency of these processes. A large number of fundamental studies on geometric, molecular, and electronic structures of solid/gas interface under ultrahigh vacuum (UHV) and geometric and molecular structures of solid/liquid interface have been carried out in the last 30 years. However, the studies on electronic structures of solid/liquid interfaces are still very limited since the techniques, which usually use electron as a probe to determine the electronic structure under UHV conditions, cannot be applicable to solid/liquid interfaces because of the presence of liquid. IR/visible double resonance sum frequency generation (DR-SFG) spectroscopy, which utilizes resonant enhancement of second-order nonlinear SFG signal with both frequency-tunable incident visible and IR lights, is a highly surface-sensitive photon-in photon-out technique, and, can therefore, readily be used for probing the interfacial electronic structures in solution.

Adsorbed CO/Pt electrochemical interface has been studied extensively because CO is an intermediate/poison of many important processes such as methanol oxidation reaction. Thus, it is a very good model system to apply and test a novel technique. In the present thesis, potential dependent DR-SFG technique was employed to obtain the information of electronic structures of CO adsorbed on various electrode surfaces, i.e., Pt(111) single crystals, polycrystalline Pt and epitaxial Pt ultrathin film deposited on polycrystalline Au substrate, in electrochemical condition, and the effect of substrate on electronic structure is discussed.

The structure of the thesis is as follows:

In Chapter 1, the introduction of surface catalysis, electrocatalysts and the related characterization techniques is given. The spectroscopic studies of CO/Pt electrochemical interface are reviewed. The basic theory of SFG spectroscopy is also introduced.

In Chapter 2, the experimental details, including the information on materials, preparation procedures of

samples, experimental setups and measurements, are provided.

In Chapter 3, the electronic structure of CO/Pt(111) interface was investigated by potential dependent DR-SFG spectroscopy in 0.5 M H₂SO₄ solution. SFG peaks corresponding to the stretching of CO adsorbed on atop site of Pt(111) were observed both at constant potential and during potential scan using eight different visible light energies. The SFG intensity increased anomalously prior to CO oxidation and the potential of the anomalous peak shifted negatively when the visible light energy decreased linearly by 1 V/eV, indicating that the origin of the anomalous increase of SFG intensity is due to the resonance of visible and/or SF light with electronic transition from the Fermi level of Pt(111) to the 5 σ_a anti-bonding state of adsorbed CO.

In Chapter 4, the electronic structure of CO/polycrystalline Pt interface was studied by using potential dependent DR-SFG technique in CO-free acid solution under constant potential control. As on Pt(111) surface, an increase of SFG intensity was found prior to CO oxidation. At a given visible energy, the SFG peak on polycrystalline Pt was observed at a little positive potential than that on Pt(111), suggesting the energy of 5 σ_a anti-bonding state of CO on polycrystalline Pt electrode is a little lower than that on Pt(111). The widths of the SFG peak with potential are broader on polycrystalline Pt electrode than that on Pt(111) electrode, showing the broader distribution of the 5 σ_a anti-bonding state of CO adsorbed on polycrystalline Pt than that on Pt(111), because of the presence of many kinds of atop sites at polycrystalline surface.

In Chapter 5, the electronic structure of CO adsorbed on a Pt sub-monolayer modified polycrystalline Au substrate prepared by electrochemically deposition method was investigated by potential dependent DR-SFG spectroscopy. As on Pt(111) and polycrystalline Pt electrodes, the SFG intensity increased prior to CO oxidation. At a given visible light energy, the potential of the SFG peak on Pt sub-monolayer modified Au electrode is more negative than that on Pt(111) and polycrystalline Pt electrodes, showing the energy of the 5 σ_a anti-bonding state of CO adsorbed on the Pt sub-monolayer modified Au electrode is higher than that on bulk Pt electrodes. This shift seems to be caused by the modulation of the d-band position by the Au substrate as suggested by a theoretical calculation. The widths of the SFG peaks on Pt modified Au are comparable to those on polycrystalline Pt but broader than those on Pt(111), reflecting the polycrystalline nature of the Pt thin film formed on the Au polycrystalline substrate.

In Chapter 6, the most important conclusions are summarized together with a brief prospect for the future work.