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Electrooxidation of Carbon Monoxide on Pd Thin Film-Coated Au Electrodes:Film Thickness Dependence

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Abstract： The adsorption and electrooxidation of CO on Pd-coated Au electrodes were studied by cyclic voltammetry and surface-enhanced Raman spectroscopy（SERS）. It is found that CO oxidation activity is film thickness dependent. Cyclic voltammograms（CVs）showed that CO oxidation peak potential shifted positively with the increase of the Pd thickness. SERS showed a redshift of the C—O stretching frequency with increasing Pd film thickness. These observations were explained by the *d*-band theory. The strain effect strengthens CO adsorption and stabilizes adsorbed CO，while the ligand effect weakens CO adsorption and eases its oxidation. The ligand effect overpowers the strain effect.

Key words： CO oxidation；Pd thin film；*d*-band theory；SERS

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Mixed-metal systems have applications in metallurgy,（electro）catalysis, and microelectronics[1]. The chemisorption properties of supported monolayers of one metal on another can be dramatically different from those of the parent metals[2], therefore providing an avenue for fine tuning the catalytic activity of that metal. The modification of the adsorption properties of the surface comes from two mechanisms：strain effect and ligand effect[3-4]. If one metal is deposited on another having a different lattice constant, strained overlayers are formed due to the average bond length difference between the metal atoms in the supported monolayer surface and those in the pure metal[3,5]. When the overlayer metal has a lattice constant smaller than that of the substrate, the metal film is under tensile strain. The *d*-orbital overlap is decreased, which results in a sharpening of the *d*-band and an upshift in its average energy（the *d*-band center）[4]. Thus, the adsorption energy of the adsorbates, such as H, O, and CO, is stronger compared with the parent

metals[4]. When the overlayer metal has a lattice constant greater than that of the substrate, the metal film is then under compressive strain and its *d*-orbital overlap is increased, which results in a broadening of the *d*-band and a downshift in its average energy[4]. Thus, the adsorption energy of the adsorbed species is weaker compared with the parent metals. Ligand effect is caused by the heterometallic bonding interaction between the overlayer atoms and the substrate, which results in a modification of the overlayer electronic structure, hence changing the surface adsorption properties[3].

The strain effect and the ligand effect on CO adsorption and oxidation have been observed experimentally. For example, in ultra high vacuum a correlation between the surface stress of Cu layer on Pd and the vibration shift of chemisorbed CO have been reported[6]. Hartmann et al reported weaker CO adsorption on Pd and PdRu films on Ru（0001）surfaces, which was attributed to the strain and ligand effects[7]. Cor-

responding studies in electrochemical environment also appeared recently. Kumar and Zou studied CO and methanol oxidation on Pt-coated Au nanoparticles with varying Pt film thickness[8]. CO oxidation peak potential is shifted negatively with increasing film thickness, which was attributed to the relaxation of the tensile strain and weakening of the ligand effect as the film becomes thicker. Du and Tong reported CO and methanol oxidation on Pt layers spontaneously deposited on Au and Ru surfaces[9]. In these studies, the ligand effect and the strain effect both strengthens CO adsorption.

　　In this work, we studied the adsorption and electrooxidation of CO on Pd-coated Au electrodes by cyclic voltammetry and surface-enhanced Raman spectroscopy (SERS). We explored the film thickness dependence of CO oxidation activity. Cyclic voltammograms (CVs) showed that the CO oxidation peak shifted positively with the increasing Pd film thickness. SERS showed a redshift of the C—O stretching frequency as the Pd film thickness increases. The observation was explained by the counteracting strain and ligand effects. To the best of our knowledge, this is the first experimental example of ligand effect working against the strain effect.

1　Experiment Section

　　Double distilled, 70% perchloric acid (HClO$_4$) was obtained from GFS Chemicals. Semiconductor grade (99.997%) carbon monoxide (CO) was obtained from Spectra gas. Palladium (II) chloride (99.999%) were purchased from Aldrich Co. All solutions were made with Milli-Q water 18.2 MΩ · cm resistivity (Milli-Q A10, Millipore). To obtain the surface-enhanced Raman effect, a Au electrode (2 mm in diameter, CH Instruments) was polished successively with 1.0 and 0.3 μm Al$_2$O$_3$ powder on a polishing cloth and roughened by electrochemical oxidation-reduction cycles in 0.1 mol · L^{-1} KCl, as described by Gao et al[10]. The Pd films on Au were prepared by a surface limiting redox replacement method[11-12]. In this method, a monolayer of Cu was first deposited on Au electrode through under-poten-

tial deposition by holding the electrode potential at 0.05 V in 1 mmol · L^{-1} CuSO$_4$ + 0.1 mol · L^{-1} H$_2$SO$_4$ solution for 4 min. Then, Cu was replaced by Pd by immersing the Cu-coated Au electrode in 5 mmol · L^{-1} PdCl$_2$ + 0.1 mol · L^{-1} HClO$_4$ solution for 10 min. Thus one nominal monolayer (ML) Pd was formed on the Au electrode surface. To obtain two monolayers Pd-coated Au electrode, the one monolayer Pd-coated Au electrode was held at 0.1 V in the 1 mmol · L^{-1} CuSO$_4$ in 0.1 mol · L^{-1} H$_2$SO$_4$ solution for 4 min to deposit a monolayer of Cu. By immersing the electrode in 5 mmol · L^{-1} PdCl$_2$ in 0.1 mol · L^{-1} HClO$_4$ solution for 10 min, a second layer of Pd was deposited. Multilayer Pd-coated Au electrode can be obtained by repeating the process above.

　　Cyclic voltammograms were recorded with an electrochemical analyzer (CHI630A, CH Instruments). SERS measurements were conducted in a two-compartment, three electrode glass cell with an optically flat glass disc as the window at the bottom. A Pt wire was used as the counter electrode and the reference electrode is a Ag/AgCl electrode with saturated KCl (CH Instruments). Cyclic voltammograms were recorded between −0.25 and +0.80 V with a scan rate of 100 mV/s in 0.1 mol · L^{-1} HClO$_4$. The electrode potential for Raman measurements was controlled by a voltammograph (CV27, BAS).

　　Raman spectra were collected with a portable micro-Raman probe system. A laser excitation at 785 nm from a diode laser was focused to a 100 μm spot on the sample with a 20 × long working distance microscope object (NA 0.42). The Raman scattering light was collected with the same objective in a backscattering fashion and sent to a monochromator. The laser power on the sample is typically 20 mW. The Raman shift axis was calibrated with a neon light. The typical spectrum acquisition time was 60 s unless otherwise noted. A 1200 groove/mm grating was used. The spectra were plotted with the intensity converted to electron counts per second (cps) and were subjected to multipoint baseline correction using the GRAMS AI program (version 7.01, Thermo Electron Corp.).

2 Results and Discussion

Fig. 1 shows the CVs of CO oxidation on Pd-coated Au electrodes as a function of film thickness. For clarity, only anodic sweeps were shown. CO oxidation was conducted in deaerated $0.1\ mol \cdot L^{-1}$ $HClO_4$ solution. The irreversibly adsorbed CO adlayer was formed by first bubbling CO into $0.1\ mol \cdot L^{-1}$ $HClO_4$ solution for 5 min while the Pd-coated Au electrode was kept at -0.2 V, followed by 10 min N_2 purging to remove solution phase CO before potential scanning. In all of the CVs, a peak appeared at positive to 0.6 V which can be attributed to the CO oxidation on the Pd surface by comparing Fig. 1 and Fig. 2. Clearly in Fig. 1, the CO oxidation peak shifts positively with the increasing thickness of Pd film, from 0.645 V on one monolayer to 0.666 V on two monolayers, and finally to 0.669 V on three and five monolayers of Pd-coated Au electrode. The positive shift of CO oxidation peak indicates that CO oxidation is more and more difficult. This observation can be explained by the d-band theory.

As discussed in the outset, the d-band center position determines the adsorption property of a metal film deposited on another metal surface. According to the d-band theory, two factors affect the d-band center position: the strain effect and the ligand effect[3]. From the strain effect, since the lattice constant of Pd (0.389 nm) is smaller than that of Au (0.408
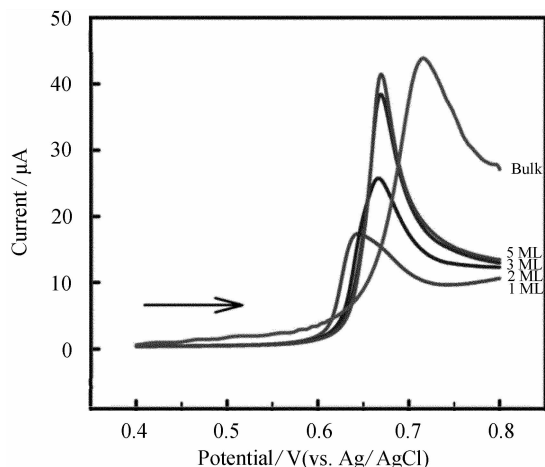

Fig. 1 CVs for CO oxidation on Pd-coated Au in $0.1\ mol \cdot L^{-1}$ $HClO_4$ solution as a function of the Pd overlayer thickness   scan rate: 100 mV/s, the arrow indicates the scan direction

nm)[13], tensile strain formed on the first Pd layer, which results in a narrower d-band width and thus an upshift of the average d-band energy. With the increase thickness of the Pd films, the effect from the tensile strain is expected to decreases[14]. The average d-band energy would then downshift to the level of the bulk Pd, which would cause a decreasing CO adsorption energy and negative shift of the CO oxidation peak potential. However, for the ligand effect, the d-band width is proportional to $r_d^{3/2}$ of each metal, where r_d is a characteristic length of a metal that is related to the spatial extension of the d-orbital of the metal[3-4]. The r_d of Pd atoms (0.094 nm) is smaller than that of Au atoms (0.101 nm)[15]. Consequently, the d-band width is greater for the first layer Pd deposited on Au then the pure Pd. Thus the d-band center decreases. As the Pd film gets thicker, the ligand effect becomes weaker. The overlayer d-band center is expected to upshift to the bulk Pd level and result in an increasing CO adsorption energy and a positive shift of the CO oxidation peak potential. The above discussion shows that the strain effect and the ligand effect on the d-band position and consequently CO oxidation potential are opposite to each other. The overall effect can be evaluated according to the following equation[3]:

$$V_i = 7.62 \sum_{j=1}^{NN} \frac{(r_d^{(1)})^{\frac{3}{2}} \times (r_d^{(2)})^{\frac{3}{2}}}{d_{ij}^5} (eV)$$

where V_i is the matrix element which is proportional to the d-band width, d_{ij} is the internuclear distance, $r_d^{(1)}$ is the r_d of Au and $r_d^{(2)}$ is the r_d of Pd, and the summation is over all of the nearest neighbor atoms.

The value of V_i depends on the structure of the surface. Given the polycrystalline nature of the surface used here, one can expect the surface structure is quite open as oppose to close packed. As an example, assuming that a Pd overlayer atom is surrounded by three Au atoms underneath and three Pd atoms on the same plane, the V_i for a Pd overlayer with such a structure is 0.21 eV, 0.05 eV higher than that of pure Pd. This simple calculation shows that the ligand effect overpowers the strain effect for Pd on Au. The

higher V_i implies broader d-band and lower d-band center energy. Thus CO adsorption energy on Pd overlayer on Au is lower than that on pure Pd and therefore easier CO oxidation which agrees with the results shown in Fig. 1. The effect gradually disappears as the film becomes thicker because of the relaxation of the strain and the disappearance of the ligand effect.

Consistent with this picture, other adsorbates on Pd-coated Au also have a lower adsorption energy compared to pure Pd as is manifested in the blank CVs. Fig. 2 shows the CVs of the anodic and cathodic sweeps after the CO stripping. The semi-reversible broad features between -0.25 V and 0.2 V are from the hydrogen adsorption (cathodic scan) and desorption (anodic scan). These current peaks increase with the Pd film thickness up to 3 ML, afterwards they remain the same. The current increase likely arises from the increase of surface roughness. At the more positive potential region in the anodic scan, the current starts to increase at ca. 0.5 V on 1 ML Pd film, signifying the oxygen adsorption and surface oxidation. The cathodic peak at ca. 0.55 V in the anodic scan is from the corresponding Pd oxide reduction. In addition to the increase of current magnitude as observed in the hydrogen adsorption/desorption region, it is noticed that the peaks of Pd oxidation and the Pd oxide reduction shift negatively with the increase of Pd film thickness. Careful inspection of the hydrogen adsorption/desorption region also reveal that H adsorption/desorption potentials shift positively. These observations suggest that the adsorption energy of hydrogen and oxygen on Pd film increases as the film becomes thicker, which again can be explained by the gradual increase of d-band center.

Evidence of stronger CO adsorption on thicker Pd film can also be found in SER spectra. Fig. 3 shows the SER spectra of CO adsorbed on Pd-coated Au electrode in 0.1 mol $\cdot$ L^{-1} HClO$_4$ solution. To form CO adlayer, the solution was first purged by N$_2$ for 5 min to remove the dissolved O$_2$ from the ambient. Then the Pd-coated Au electrode was kept at -0.2 V for 5 min with CO bubbling, followed by 10 min N$_2$ purging to remove solution phase CO. After that, the

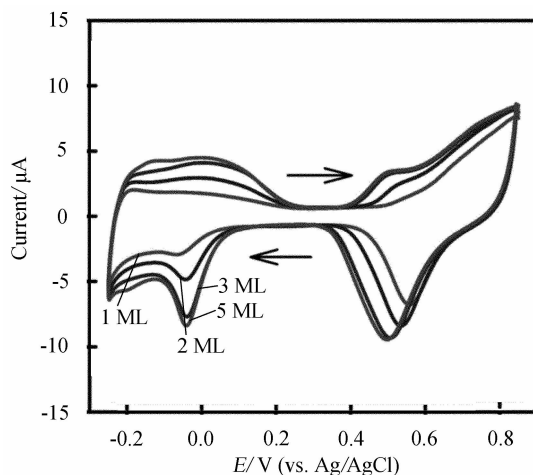Fig. 2　CVs of Pd-coated Au in 0.1 mol $\cdot$ L^{-1} HClO$_4$ solution as a function of Pd film thickness　scan rate: 100 mV/s, the arrows indicate the scan direction

potential stepped positively to 0.0 V and was held at this potential for the period of SER spectrum acquisition.

Two peaks are clearly evident in the C—O stretching (ν_{CO}) frequency region. The peak with frequency around 1964 cm^{-1} arises from the bridge-bound CO on Pd and the peak at around 2060 cm^{-1} can be assigned to the atop CO on Pd[16-18]. As the film thickness increases, the Raman band intensity decreases, similar to the previous reports[12,17,19]. The decreasing intensity is largely due to the weakening of the electromagnetic field enhancement resulted from the increasing distance of the adsorbate from the Au substrate which is mainly responsible for the Raman enhancement[19-20]. From Fig. 3, the measured bridging CO stretching frequency gradually decreases from 1964 cm^{-1} at one monolayer of Pd to 1959 cm^{-1} at five monolayers of Pd. This change reflects the influence of Pd film thickness on the Pd-CO bonding. The bonding of CO on Pd surface can be described as σ donation from CO molecule to metal d-band and π back donation from metal d-band to π^* orbital of CO molecules[6,18]. The π back donation into the anti-bonding molecular orbital weakens the C—O bond, which causes the C—O stretching shifts to the lower frequency. The π back donation is determined by the d-band center level: the higher the d-band center, the easier the π back donation. As discussed above, as

the film thickness increases, the d-band center moves up, resulting in a stronger π back donation and increasing CO adsorption energy. Thus the ν_{CO} shifts to lower frequency. The strengthening CO-Pd bond with increasing Pd film thickness agrees well with the CV results shown in Fig. 1.
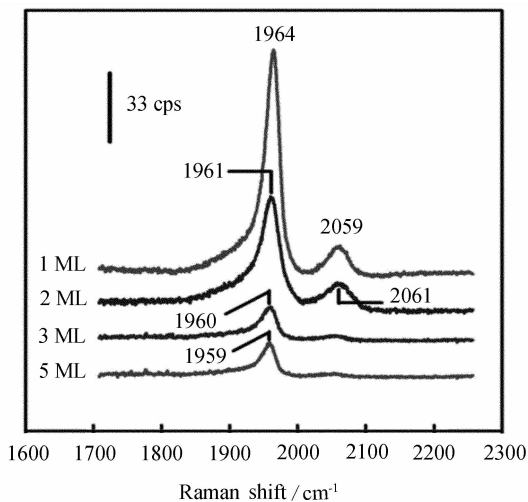

Fig. 3　Surface-enhanced Raman spectra of CO adsorbed on Pd-coated Au in 0. 1 mol · L^{-1} HClO$_4$ solution as a function of Pd overlayer thickness
the applied potential is controlled at 0. 0 V

3　Conclusions

Adsorption and electrooxidation of carbon monoxide on Pd-coated Au electrodes were studied by cyclic voltammetry and surface-enhanced Raman spectroscopy. The thickness of Pd film was varied from one to five monolayers to examine the effects of film thickness on chemical properties of the metal overlayer. CVs showed a positive shift of CO oxidation peak position for CO oxidation on Pd. The results were explained by the d-band theory. The combination of strain effect and ligand effect causes the increase of the d-band center for the Pd film with increasing film thickness, which strengthens the Pd-CO bond and consequently the positive shift of the CO oxidation peak. Consistent with the CV results, SER spectra showed a redshift of the ν_{CO} with the increasing Pd film thickness, which indicates a weakened C—O bond and strengthened metal-C bond. These results show that the electrocatalytic activity of a metal can be changed by forming thin films on another metal.

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一氧化碳在钯薄膜修饰的金电极上的 电氧化-厚度的影响

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摘要： 采用扫描循环伏安法及表面增强拉曼散射光谱研究了一氧化碳(CO)在钯修饰金电极上的吸附与氧化. 结果表明 CO 氧化电位随钯膜厚度增加而正移,同时 C—O 伸缩振动频率红移. 本文利用 d 能带理论解释观察现象. 应力效应使 CO 吸附变强,难以氧化;但配体效应使 CO 吸附变弱,易于氧化. 在薄膜中配体效应强于应力效应.

关键词： CO 电氧化；Pd 薄膜；d 能带理论；表面增强拉曼散射