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Nonlinear Stark effect observed for carbon monoxide chemisorbed on gold core/palladium shell nanoparticle film electrodes, using in situ surface-enhanced Raman spectroscopy

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ABSTRACT

The potential (E)-dependent vibrational behavior of a saturated CO adlayer on Au-core Pd-shell nanoparticle film electrodes was investigated over a wide potential range, in acidic, neutral, and basic solutions, using in situ surface-enhanced Raman spectroscopy (SERS). Over the whole of the examined potential region (-1.5 to 0.55 V vs. NHE), the peak frequencies of both the C–O_M and the Pd–CO_M band (here, M denotes the multiply-bonded configuration) displayed three distinct linear regions: dv_{C-O_M}/dE decreased from ~ 185 – 207 (from -1.5 to -1.2 V) to ~ 83 – 84 cm^{-1}/V (-1.2 to -0.15 V), and then to 43 cm^{-1}/V (-0.2 to 0.55 V); on the other hand, dv_{Pd-CO_M}/dE changed from ~ -10 to -8 cm^{-1}/V (from -1.5 to -1.2 V) to ~ -31 to -30 cm^{-1}/V (-1.2 to -0.15 V), and then to -15 cm^{-1}/V (-0.2 to 0.55 V). The simultaneously recorded cyclic voltammograms revealed that at $E < -1.2$ V, a hydrogen evolution reaction (HER) occurred. With the help of periodic density functional theory calculations using two different (2×2)-3CO slab models with Pd(111), the unusually high dv_{C-O_M}/dE and the small dv_{Pd-CO_M}/dE in the HER region were explained as being due to the conversion of CO_{ad} from bridge to hollow sites, which was induced by the co-adsorbed hydrogen atoms formed from dissociated water at negative potentials.

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1. Introduction

The potential-dependence of metal-adsorbate bonding at the electrochemical interface is an issue of basic importance in electrochemistry. One of the most extensively studied topics in this area is the vibrational Stark effect (a change in the vibrational frequency with respect to the applied electric field) of CO on platinum-group metal surfaces [1–4]. It is known that the observed Stark-tuning rates are sensitive to changes in the

electrode materials [2,5], adsorbate coverage [5], binding geometry [6–8], and co-adsorbed species [6–9]; however, the mechanism responsible for the Stark effect remains a topic of debate [10]. One of the challenges commonly encountered is that it is impossible to find a system where the adsorbate coverage, adsorption sites, and the orientation of the system are constrained to a specific case as the potential is altered. Consequently, contributions to the band frequency changes from variations in the dipole-dipole coupling effects, and other

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structure-dependent interactions, cannot be avoided [7,11].

Previous studies have investigated CO adsorption at a Pd electrode using electrochemical infrared adsorption spectroscopy (EC-IRAS) [8,12–15]. From the well-defined C–O stretching vibration, it has been confirmed that CO can adsorb at atop (CO_L), 2-fold bridge (CO_B), and 3-fold hollow (CO_H) sites. In this case, a linear Stark slope of the C–O stretching vibration ($d\nu_{\text{C-O}}/dE \approx 40 \pm 10 \text{ cm}^{-1}/\text{V}$) is observed in acidic solutions [8,15].

Although these studies have clarified the behavior in this system, difficulties remain because there is no direct correlation between the CO adsorption energy and the C–O stretching frequency, because of the alteration of the spectral behavior of the C–O stretching band by the strong dipole-dipole coupling effects between the nearby CO_{ad} molecules. The dipole-dipole coupling effects for the metal–CO vibration are much weaker than those for the C–O vibration [16]. Information on Pd–CO stretching cannot be obtained in electrochemical environments using EC-IRAS, because of the limited transparency of the IR window (normally $> 800 \text{ cm}^{-1}$), and the strong absorption in the far-infrared region by water, which is typically used as the solvent in such studies. In contrast, surface-enhanced Raman spectroscopy (SERS) can be used to obtain vibrational information in a wide spectral window ($5\text{--}4000 \text{ cm}^{-1}$), and does not require the use of the spectral-difference method to remove solution-phase interferences. However, few electrochemical in-situ SERS studies have been carried out on CO adsorption on Pd substrates, because SERS studies on pure roughened Pd electrodes are typically limited by the poor surface sensitivity. Zou et al. [2] studied the Stark effects of CO adsorption on Pd film-coated Au electrodes by borrowing the strong SERS enhancement from the Au substrate, and found that the slope for the Pd–CO stretching vibration ($d\nu_{\text{Pd-CO}}/dE$) was roughly linear ($\sim 10 \text{ cm}^{-1}/\text{V}$). However, because of the limited range of potentials applied in the above studies, it is difficult to infer how the external electric field effect influenced the adsorption behavior for CO_{ad} at the Pd electrodes.

Here, we report potential-dependent vibrational Stark behavior, based on surface-enhanced Raman measurements of a CO adlayer at an Au-core/Pd-shell nanoparticle film electrode in acidic, neutral, and basic aqueous media, in a broad potential region from -1.5 to 0.55 V . The potential range accessible for SERS measurements is determined by the onset of CO_{ad} oxidation and a strong hydrogen evolution reaction (HER); the potential range can be expanded by using different electrolytes. Our results revealed distinct Stark slopes in three different potential regions, with a pronounced increase in $d\nu_{\text{C-O}}/dE$, and a decrease in $|d\nu_{\text{Pd-CO}}/dE|$ (the absolute value of $d\nu_{\text{Pd-CO}}/dE$) at potentials where the HER reaction occurred. Such spectral behavior was preliminarily attributed to the CO_{ad} site transition induced by the co-adsorbed hydrogen atoms involved in the HER, as confirmed using periodic density functional theory (DFT) calculations.

2. Experimental and computational

2.1. Experimental set-up

The design of the electrochemical flow cell used in the present SERS study has been described in detail elsewhere [17]. The electrolyte flowing through the cell could be switched between different electrolytic reservoirs, where the flow rate was controlled by changing the hydraulic pressure. In this experiment, the flow rate was $50 \mu\text{L}/\text{s}$. All measurements were performed at ambient temperature ($25 \pm 3 \text{ }^\circ\text{C}$). A thin Au foil (thickness $50 \mu\text{m}$) and a saturated calomel electrode (SCE) were used as the counter electrode (CE) and the reference electrode (RE), respectively. Here, all potentials are reported with respect to normal hydrogen electrode (NHE).

Electrochemical measurements were conducted using a CHI631B electrochemical workstation (CH Instruments, Shanghai, China). SERS measurements were carried out using a confocal microprobe Raman system (LabRam I from Dilor, France), using an air-cooled CCD and a He-Ne laser operating at 632.8 nm . The laser power delivered at the sample (with beam diameter of ca. $2 \mu\text{m}$) was approximately 5 mW . The microscope attachment was based on an Olympus BX40 system, using a long working length (8 mm) $\times 50$ objective. A $1800 \text{ g}/\text{mm}$ grating was used, and the spectral resolution was 1 cm^{-1} .

2.2. Chemicals, and preparation of 55 nm Au@0.7 nm Pd nanoparticle film electrodes

PdCl_2 (99.9%), HAuCl_4 (AR), HCl (AR), sodium citrate (AR), ascorbic acid (AR), Na_2SO_4 (AR), H_2SO_4 (GR), and NaOH (GR) were purchased from Shanghai Reagent Corporation, China. Millipore Milli-Q Water ($18.2 \text{ M}\Omega/\text{cm}$) was used throughout the study. Before SERS measurements, all of the electrolyte solutions were deaerated via continuous N_2 (4N, Linde Gas China) purging. CO-saturated solutions were achieved by pre-bubbling the supporting electrolyte with pure CO (99.9%, Linde Gas China) for 15 min in the electrolyte reservoir, and via continuous purging during the experiments.

55 nm Au@0.7 nm Pd nanoparticles were prepared by coating a thin layer (0.7 nm) of Pd over 55 nm Au nanoparticles, following the procedure reported by Tian's group [18]. First, a H_2PdCl_4 ($1.0 \text{ mmol}/\text{L}$) aqueous solution was prepared by dissolving 88.6 mg of PdCl_2 in 11 mL of $0.1 \text{ mol}/\text{L}$ HCl under heating and stirring, and diluting the resulting solution to a final volume of 500 mL . Then, 30 mL of a sol containing 55 nm Au seeds was mixed with 0.8 mL H_2PdCl_4 ($10 \text{ mmol}/\text{L}$) solution for several minutes, after synthesizing the Au nanoparticles with a diameter of ca. 55 nm by reducing AuCl_4^- using sodium citrate. 0.4 mL ascorbic acid ($10 \text{ mmol}/\text{L}$) solution was slowly dropped into these mixtures under vigorous stirring, using a syringe controlled by a step motor. The mixtures were further stirred for approximately 20 min, to ensure the complete reduction of the H_2PdCl_4 . The 55 nm Au-core 0.7 nm Pd-shell (denoted as 55 nm Au@0.7 nm Pd or Au@Pd hereafter) sol was centrifuged three times, to remove excess reactants. The remaining sol ($5 \mu\text{L}$) was then cast on a smooth Pd electrode (diameter ca. 1.5 mm), and dried in a desiccator. This procedure was repeated three times, to ensure that the Pd electrode was completely covered with the Au@Pd nanoparticles. The nanoparticles displayed an ellipsoidal shape with a uniform

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