

Surface dynamics of CO adsorption on electrode of nanometer scale Pt thin film investigated by *in situ* time-resolved FTIR spectroscopy

Zhi-You Zhou, Di Si, Shi-Gang Sun*

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, Xiamen University, Xiamen 361005, China

We have discovered recently the abnormal infrared effects (AIREs) of nanometer scale thin film of platinum group metals and alloys in chemisorption [1]. The inversion of the IR band direction and the enhancement of IR absorption of adsorbates in AIREs reinforced the ability of *in situ* IR spectroscopy in studies of electrode surface processes. In the present paper, we have developed an *in situ* time-resolved FTIR spectroscopy (TRFTIRS), and applied to study the dynamics of surface process of CO adsorption at an electrode of nanometer scale thin film of platinum supported on glassy carbon (nm-Pt/GC). Thanks to the AIREs of nm-Pt/GC the dynamics of transformation of bridge bonded (CO_B) to linear bonded CO (CO_L) or vice versa has been studied for the first time.

The diagram of setup of TRFTIRS is shown by Fig.1. A step-scan FTIR spectrometer (Nexus 870, Nicolet) was employed in the study. The timing schema for step scan time-resolved spectroscopic (TRS) data collection is illustrated in Fig.2. A homemade signal synchronizer was used to trigger electrode potential in order that the TRS data collection can be synchronized with electrode polarization. As shown in Fig.2, the laser signal and the trigger signal of the spectrometer are input into the signal synchronizer, generating a potential pulse between two potentials E_1 and E_2 . The laser signal is used to trigger electrode potential to E_1 , at which the static single-beam spectrum ($R(E_1)$) is collected. The trigger signal from the spectrometer is employed to switch electrode potential to E_2 , where the TRS single-beam spectra ($R(E_{2,t})$) are collected in time sequence. In the case of CO adsorption on nm-Pt/GC electrode in 0.1 M NaSO₄ solution, the E_1 and E_2 are chosen respectively at -0.95 and -0.50 V(SCE). It is known that CO_{ad} at both potential is stable at nm-Pt/GC surfaces, but is mainly in CO_B at -0.95V and in CO_L at -0.50 V [2]. After having completing the

TRS collection procedure a reference single-beam spectrum ($R(E_R)$) is collected at 0.30V, at which CO_{ad} is oxidized completely into CO₂ species. The *in situ* TRFTIRS spectra are then defined as,

$$\frac{\Delta R}{R}(t) = \frac{R(E_{S,t}) - R(E_R)}{R(E_R)}$$

The $R(E_1)$ and $R(E_{2,t})$ are taken both as $R(E_{S,t})$. A series of *in situ* TRFTIR spectra are displayed in Fig 3. We observed that the intensity of CO_L is increased quickly when electrode potential is stepped from -0.95 to -0.50 V, illustrating the dynamic process of the transform of CO_B to CO_L at nm-Pt/GC surface.

The preliminary results demonstrated the success of establishment of the *in situ* TRFTIRS technique, and the possibility of studying the dynamics of electrode surface processes at a short time scale.

References:

- [1] G.Q. Lu, S.G. Sun. et al. *Langmuir*, 2000, **16**: 778.
- [2] G.Q. Lu. Ph.D. Thesis, Xiamen University, 1997.

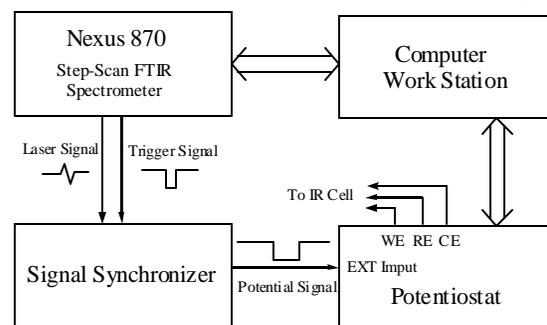


Fig.1 Diagram of setup of *in situ* TRFTIRS

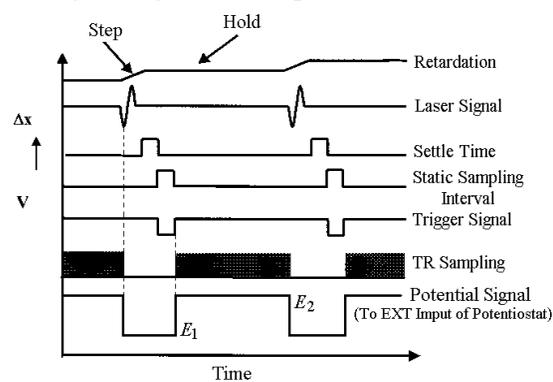


Fig.2 *In situ* TRFTIRS data collection signals

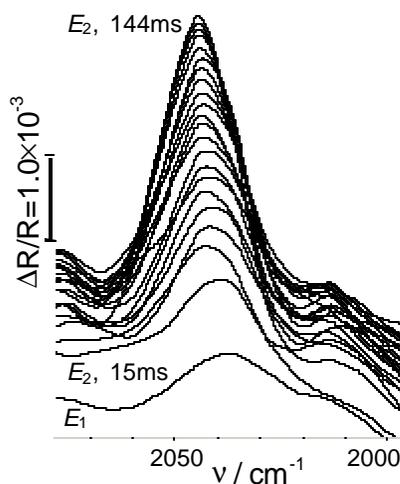


Fig.3 *In situ* TRFTIR spectra of CO adsorbed on nm-Pt/GC electrode, 0.1M Na₂SO₄ solution, $E_1 = -0.95V$, $E_2 = -0.5V$, $E_R = 0.3V(SCE)$.

* Correspondence author, Fax: +86 592 2183047, Email: sgsun@xmu.edu.cn