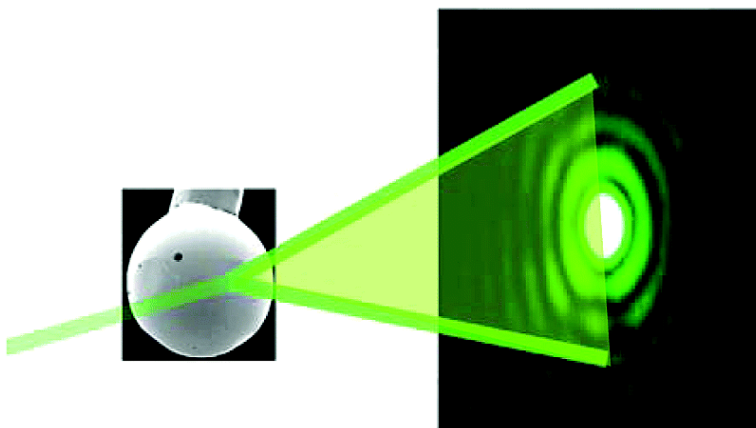


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Dynamics of a Surface Phase Transition As Monitored by in Situ Second Harmonic Generation

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The advent of an array of scanning probe microscopies¹ and synchrotron-based surface X-ray diffraction (SXR) techniques² has opened exciting new prospects for monitoring in situ changes in the arrangement of atomic and molecular species at solid–gas and solid–liquid interfaces, including those induced by an externally applied potential.^{3–5} Although considerable insight has been gained into static aspects of such interfacial structural transformations, as surface reconstructions⁶ and phase transitions,^{7–10} the factors that govern their dynamics still remain to be elucidated. At least two problems have hampered progress in this specific area: the scarcity of suitable probes endowed with high sensitivity, specificity, and temporal resolution, and the lack of reliable methods for the preparation and characterization of clean, well-ordered metal surfaces of small enough dimensions to reduce the total interfacial capacity, and thus the overall RC time constant of the electrochemical cell. Optical methods in the UV–visible region offer extraordinary advantages for studies of this type, as most solvents are transparent to light in this energy range. Most importantly, minute modifications in the electronic properties of the interface, such as those derived from changes in its state of charge, or in the coverage of adsorbed species, often elicit corresponding changes both in the linear and in the nonlinear optical properties of the interface, as in the electroreflectance (ER) effect,¹⁰ and second harmonic (SHG),^{11–13} sum (SFG), and difference frequency generation (DFG),¹⁴ respectively.

The present contribution examines the dynamics of a surface phase transition involving adsorbed CO on Pt(111) microfacets formed spontaneously on the surface of single-crystal microspheres,¹⁵ in CO-saturated 0.1 M HClO₄ aqueous solutions, using potential step-SHG. As originally reported by Villegas et al.,⁹ in situ STM images of CO adsorbed on Pt(111) surfaces in this medium are consistent with the presence of a hexagonal close-packed (2 × 2)-3CO adlayer (CO coverage, $\theta_{\text{CO}} = 0.75$) at potentials $E < 0$ versus SCE. In situ STM images recorded at $E > 0$, but negative to the onset of oxidation of the entire adsorbed CO monolayer, revealed formation of a different superstructure identified by these workers as $(\sqrt{19} \times \sqrt{19})R23.4^\circ - 13\text{CO}$ ($\theta_{\text{CO}} = 13/19 \approx 0.68$). Although more recent in situ SXR data reported by Lucas et al.¹⁶ do not seem to support the existence of this latter superstructure, consensus has been reached that a new phase, to be denoted hereafter as dilute, does form under these conditions and that the process is reversible in CO-saturated solutions.

Indeed, further evidence for the reversible nature of the (2 × 2)-3CO ↔ dilute CO-Pt(111) phase transition was obtained by Akemann et al.,^{17,18} who observed large enhancements (ca. 50%) in the intensity of SHG signals, $I(2\omega)$, recorded in situ at potentials at which the dilute phase is formed. Also noticed by these authors was a slight difference in the $I(2\omega)$ versus E curves for potential scan-hold experiments in the positive and negative directions over the region in which the phase transition ensues. This overall behavior was reproduced in our laboratory by monitoring $I_{\text{p,p}}(2\omega)$

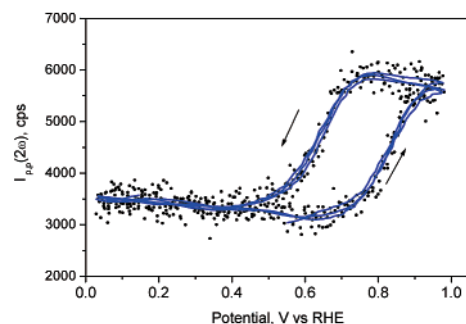


Figure 1. Plot of three consecutive $I_{\text{p,p}}(2\omega)$ (8-point average) vs potential curves obtained from a Pt(111) microfacet electrode in CO-saturated 0.1 M HClO₄(aq) during a linear potential scan (10 mV/s) over the range in which the (2 × 2)-3CO ↔ dilute phase transition occurs.

versus E (where p,p refers to the polarization state of the incident and SHG light, respectively) from Pt(111) microfacets, while scanning E continuously at 10 mV/s (see Figure 1), except that the transition in this case was found to occur over a much wider potential range, ca. 120 mV. Although the physicochemical bases of the enhancement in $I_{\text{p,p}}(2\omega)$ induced by formation of the dilute phase are not known at present, the difference in the magnitude of $I_{\text{p,p}}(2\omega)$ between the two phases provides a basis for monitoring the dynamics of the transition via potential step-time-resolved SHG methods.

The instrumental setup used for transient SHG measurements has been described in detail elsewhere.^{15,19} For these specific experiments, the Pt electrode was initially polarized at a potential within the range in which the (2 × 2)-3CO adlayer forms on the (111) microfacets, that is, $50 < E_{\text{CO}(2 \times 2)} < 400$ mV, followed by a potential step to a value at which CO, under either static or slow-scan conditions, is present in the dilute phase, that is, $0.85 < E_{\text{dil}} < 0.9$ V. In light of the disparate time constants of the forward, that is, (2 × 2)-3CO → dilute (slow, few hundreds of a millisecond) and reverse processes, that is, dilute → (2 × 2)-3CO (fast, few tens of a microsecond), the duty cycle of the potential step sequence was carefully adjusted to allow for the dilute phase to fully reconstitute, that is, for $I_{\text{p,p}}(2\omega)$ to reach a plateau, before E was stepped back to $E_{\text{CO}(2 \times 2)}$, and thus reset the system before the next acquisition. For studies of the dynamics of the much faster reverse transition, the overall time resolution was increased; that is, the bin size was decreased from 1.3 ms to 40 μs, and the time window of observation was adjusted using the features of the pulse delay box. Plots of $I_{\text{p,p}}(2\omega)$ versus time for potential steps between 0.04 and 0.913 V versus RHE, (2 × 2)-3CO → dilute (130 coadded acquisitions) and between 0.913 and 0.04 V dilute → (2 × 2)-3CO (833 coadded acquisitions), shown in the upper and lower panels in Figure 2, respectively, clearly indicate that the forward transition is ostensibly slower than its reverse counterpart. Although it becomes possible in certain cases to extract quantitative coverage information from SHG data, it is not clear whether the stringent

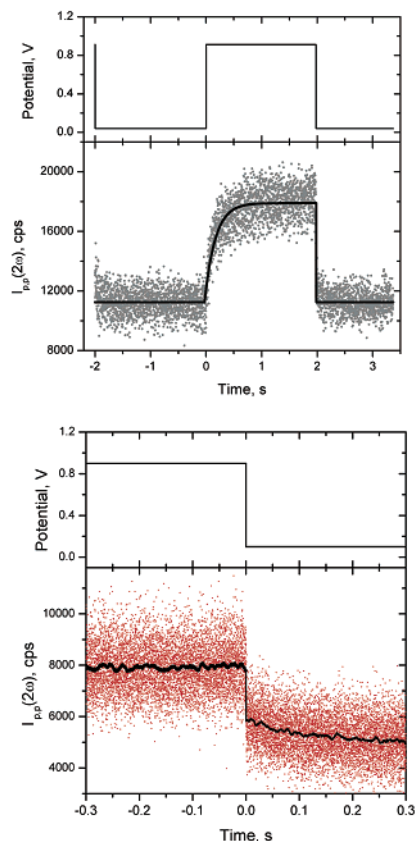


Figure 2. Upper panel: Plots of $I_{p,p}(2\omega)$ vs time collected by stepping the potential between 0.04 V, that is, (2×2) -3CO, and 0.913 V vs RHE, that is, dilute phase, under otherwise the same conditions as those specified in Figure 1 (bin size: 1.3 ms). The scattered points represent the coadded average of 130 acquisitions, and the solid line is the best statistical fit to these data (see text). Lower panel: Plots of $I_{p,p}(2\omega)$ vs time collected by stepping the potential between 0.9 V (2×2) -3CO and 0.1 V vs RHE, dilute phase, under otherwise the same conditions as those specified in Figure 1 (bin size: 40 μ s). The scattered points represent the coadded average of 883 acquisitions, whereas the solid line is the corresponding 100-point average.

requirements involved²⁰ are met by the system under study. Instead, the $I_{p,p}(2\omega)$ versus time curve for the forward process was simply fit to an exponential function of the type $A_0(1 - \exp[-t/\tau_1])$, yielding a time constant τ_1 of ca. 0.19 s, with the process being completed in about 1 s. In stark contrast, the reverse process, that is, dilute $\rightarrow c(2 \times 2)$, appears to consist of a fast stage (shorter than 40 μ s), which constitutes ca. 75% of the total signal change, followed by a much slower decay, which can be approximated by an exponential function of the type $B \exp[-t/\tau_2]$, yielding a τ_2 of ca. 0.1 s. Although this latter stage could reflect diffusion limitations due to depletion of solution-phase CO during polarization at the much higher potential, the change in θ_{CO} involved is so small that adsorption hindrances cannot be ruled out.

Careful inspection of voltammetric curves obtained with massive Pt(111) crystals in other laboratories^{17,18} indicate that, in the region in which the forward transition occurs, the current increases, suggesting that the decrease in θ_{CO} is caused by electrooxidation, rather than simple desorption of CO. On this basis, the rather slow increase in $I_{p,p}(2\omega)$, which accompanies the (2×2) -3CO \rightarrow dilute phase transition, would be consistent with a corresponding slow decrease in θ_{CO} caused by activated electrooxidation of adsorbed CO, a process that requires the presence of oxygenated species, such as adsorbed hydroxyl ions, in neighboring sites.²¹ In fact, the number of defects on spontaneously formed microfacets of the type employed in this work is expected to be minimal; hence, the temporal signals being monitored reflect, in all likelihood, rates of propagation of the phase transition triggered not on the Pt(111) facet itself, but on areas of the microsphere external to it. Support for this view is provided by the much faster rates for the forward transition observed by Akemann et al.^{17,18} for cut single crystals, which are expected to display a much larger number of defects. In contrast, the reverse transition, that is, (2×2) -3CO \rightarrow dilute phase, involves simple adsorption of CO and thus, except for steric hindrances, should be comparatively very fast, as the data shown in the lower panel Figure 2 indicate.

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