Excitation Wavelength Dependent Three-Wave Mixing at a CO-Covered Platinum Electrode

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The interfacial electronic structure of a CO-covered polycrystalline platinum electrode has been studied by using the optical second harmonic generation (SHG) and sum frequency generation (SFG) techniques with various excitation wavelengths. Although the nonlinear optical (NLO) signal was enhanced by the absorption of CO at all excitation wavelengths employed in this study, the potential dependent behaviors of the NLO signal were different between the near-infrared excitation and the visible excitation. The difference was attributed to the different mechanisms for the enhancement of the NLO signal. While the electron transition from the Fermi level of Pt to the unoccupied 2π* orbital of adsorbed CO was considered to be coupled with the NLO photon in the case of visible excitation, the dc field induced SHG regime was applied to the result obtained by the near-infrared excitation.

Introduction

The electrochemical oxidation of small organic molecules, e.g., methanol, formaldehyde, and formic acid, at a platinum electrode is a technologically important catalytic process that is utilized in future energy technology, e.g., direct methanol fuel cell. It is well-known that the adsorbed CO (CO(a)) which is formed dissociatively from a parent molecule behaves as a poison for the direct oxidation of the parent molecule and other electrochemical reactions.1–12 Accordingly, knowledge about the mechanisms of both the absorption and the oxidation of CO(a) is very important from the industrial point of view. The fundamental aspects of electrochemical surface science are concerned with the microscopic understanding of the bonding and the reactivity of adsorbates which are influenced by morphological and electronic structures of the interface. CO(a) on Pt is one of the ideal adsorbates in this respect because much information has been obtained by UHV studies.13–18 The electrochemical behavior of the CO/Pt system has been investigated by using various techniques including infrared reflection absorption spectroscopy (IRAS),6–11,19–27 differential electrochemical mass spectrometry (DEMS),28–30 electrochemical quartz crystal microbalance (EQCM),31 and surface-enhanced Raman scattering (SERS).32–34 Although these methods are very powerful for the quantitative analysis of the adsorbate and investigation of the oxidation mechanism, they cannot provide direct information about interfacial electronic structure.

Three-wave-mixing processes such as optical second-harmonic generation (SHG)35 and optical sum frequency generation (SFG)36 have been recognized as novel in situ optical probes of surface electronic and geometric structures. Optical SHG is one of the second-order nonlinear optical effects, and it is the conversion of two photons of frequency ω into a single photon of frequency 2ω with laser irradiation. In the electric dipole approximation, even order nonlinear optical effects require noncentrosymmetric media. Thus, SHG cannot be observed in centrosymmetric media such as bulk metals and solutions and at interfaces between two centrosymmetric media. The SHG process can occur only within a few atomic layers of both sides of the interface where inversion symmetry is broken. Consequently, the SHG signal is sensitive to changes at the surface and interface, and therefore, the SHG process is a useful probe of various interfacial phenomena. This technique has been applied to various systems including electrochemical systems to probe the dc field33–36 and geometric and electronic structure of interfaces,37–42 and is often used to study the adsorption of molecules, ions, and metal atoms on various interfaces in both resonant and nonresonant conditions.32,40–42 The resonant enhancement of the SHG signal is observed when the electronic transition couples energetically with either the input photon or the output SH photon. The surface electronic structures of semiconductors32–34 and metals45–49 and molecular electronic transitions at liquid/gas and liquid/liquid interfaces50–52 have been investigated by utilizing this effect. The resonant SHG signal should be dominated by interfacial features of the specific chemical species, and therefore, the analysis of the resonant SHG profile should provide a simple picture of interfacial phenomena. On the other hand, nonresonant SHG53–55 is an indirect probe of interfacial phenomena via perturbation and redistribution of the surface electronic structure as a result of absorption and requires a complex analysis of the signal. This approach is most useful to study electron-rich surfaces such as metals and semiconductors.

SFG is inherently the same process as SHG. In SFG, two photons of frequency ω1 and ω2 are converted into a single photon of frequency ω1+ω2. Actually, SHG can be considered as the special case of SFG when ω3 = ω2. Although the optical SFG technique has been mostly applied to the vibrational spectroscopy at surfaces and interfaces,56–58 it has been also used to supplement electronic SH spectroscopy in a few studies.59–61 Since SH enhancement can take place by resonant transition at surfaces with either the incident fundamental or generated SH photons, one cannot distinguish which photon contributes to the resonance. This problem should be solved and the resonant energy can be determined using the SFG technique together with the SHG technique. For example, Heinz et al. carried out both SHG measurements with tunable visible light from a dye laser and SFG measurements with...
tunable visible light and fixed near-infrared light to study a CaF$_2$/Si(111) interface and found that the resonant line was observed at the same visible input wavelength. Since the SH wavelength was different from the SF wavelength with the same input visible light, the resonance at the visible input wavelength was confirmed. In addition, SFG can extend the wavelength region to be investigated, although the experimental simplicity of SHG is weakened.

In our previous publications, we applied the optical SHG technique to study the electrochemical oxidation of formaldehyde on a Pt electrode at 532 nm excitation and found that the SHG response was sensitive to the existence of CO(a). We proposed that the electron transition resonance was important in the SHG of this particular case, although it was not clear whether the fundamental photon or the SH photon was energetically coupled with the electronic transition and what states were associated with the resonance.

In this paper, we carried out wavelength dependent SHG experiments of CO(a) on a Pt electrode at several excitation wavelengths and examined the resonance scheme making reference to the UHV studies in order to clarify the mechanisms for the SHG enhancement. SFG measurements were also carried out to extend the wavelength region to be investigated.

Experimental Section

Nonlinear Optical Measurement. Two different light sources were used to create a nonlinear optical (NLO) signal on the electrode surface. One was a 10 Hz Q-switched Nd: YAG laser (LEXEL, HY-200S), and the other was an optical parametric oscillator (OPO: Lambda Physik, Scan Mate OPPO) pumped by third-harmonic light (354.8 nm) from a dipole-pumped Nd:YAG laser (Coherent, Infinity 40–100). The NLO spectrum over the broad photon energy range was obtained by combining two different interfacial nonlinear optical methods. SHG measurement with the signal light (520 nm < $\omega_1$ < 680 nm) from the OPO provided information within the energy range 260 nm < 2$\omega_1$ < 340 nm, and SFG measurement with the signal light (520 nm < $\omega_1$ < 640 nm) from the OPO and fundamental light ($\omega_2$ = 1064 nm) from the YAG laser provided information in the energy range 350 nm < $\omega_1$+$\omega_2$ < 400 nm. SHG measurement covered the wavelength region where the intensity of visible light from the OPO was too low to create the detectable SHG signal. SHG measurement with the fundamental light (1064 nm) from the YAG laser was also carried out to measure a near-infrared excited SHG response.

Figure 1a shows the experimental arrangement for the SHG measurement for 1064 and 532 nm excitation. The excitation beam was slightly focused onto the surface of a platinum electrode in a spectroelectrochemical cell with angle of incidence at 60°. The fluencies of the excitation were 10 mJ/pulse for the 1064 and 532 nm excitation. The SHG signal was normalized to the excitation light intensity. The polarization of the excitation beam was set with a combination of a polarizer and a double Fresnel rhomb, and the polarization of the SH light was selected by another polarizer. All the nonlinear optical data reported in this paper were obtained with the p-in/p-out polarization condition.

Experimental arrangements for the SHG and SFG measurements using the OPO/YAG light source were essentially the same as that described above with minor differences. In these cases, the square of the intensity of the partially reflected fundamental light was used as a reference signal. A combination of a double Fresnel rhomb and a Glan-laser polarizer was used not only to set the input polarization but also to control the input laser power at various wavelengths from the OPO to be constant. The fluencies of the excitation were <2 mJ/pulse for the visible SHG measurement. In the case of the SFG measurement, the near-infrared beam from the YAG laser was set on the same beam path of the visible beam from OPO by means of the proper harmonic separation mirrors, and sum fluencies of the excitation beams were <3 mJ/pulse.

Electrochemistry. A 1 mm diameter platinum disk held in a Kel-F holder (the apparent electrode diameter: 8 mm) was used for the electrochemical NLO measurement. This electrode was polished with alumina powder, which was exchanged successively to smaller grades down to 0.05 µm, to be optically flat and was sonicated in deionized water before it was introduced in a spectroelectrochemical cell.

Water purified by the Milli-Q system and as-received perchloric acid (reagent grade, Wako Pure Chemicals) were used to prepare the electrolyte solution. Deaeration of the solution was carried out by bubbling the high-purity nitrogen (> 99.99%) through the electrolyte solution. CO-saturated solution was prepared by passing CO gas through the electrolyte solution in the spectroelectrochemical cell. The electrode potential was controlled with an electric polarization unit (Toho Tech. Res., PS-07). The electrode potential, the current, and the normalized SHG signal were converted to digital values via an a/d converter and stored on a personal computer (NEC, PC-9801R5).

A standard three-electrode configuration was constructed with an Ag/AgCl (saturated NaCl) reference electrode and a Pt counter electrode. After the introduction of the working electrode to the spectroelectrochemical cell, the electrochemical cleaning cycles, which consisted of continous potential cycling between −0.2 and +1.2 V in 0.1 M HClO$_4$ solution, were performed before each electrochemical SHG experiment until the cyclic voltammogram (CV) became that of a clean platinum electrode.

The experimental sequence for the electrochemical NLO experiments was as follows and is described in Figure 1b. In the course of the potential sweep in the 0.1 M HClO$_4$ solution, the potential scan was stopped at $E_{ads}$, and then, CO gas was introduced to the spectroelectrochemical cell through a Teflon tube. After 5 min, CO remaining in the solution was removed by bubbling nitrogen gas through the electrolyte solution for 15 min, and then, the potential was swept in the positive direction. Consequently, CO should exist only on the platinum surface at the initial stage of the experiments and the influence on the NLO response by the adsorption of excess CO was avoided.

Results

Figure 2 shows typical results of the cyclic voltammogram (a) and the potential dependent profiles of the SHG signal excited at 532 nm (b) and 1064 nm (c) at a bare Pt electrode in
0.1 M HClO₄ solution. At both excitation wavelengths, the enhancement of SHG with the formation of underpotentially deposited hydrogen (upd-H) in the negative potential region was observed. These potential dependences are similar to that obtained at Pt electrodes with 604 nm excitation by Corn and his co-workers.⁶⁵,⁶⁶ They introduced the resonant mechanism idea to explain the SHG enhancement with the adsorption of hydrogen on Pt. Although a similar potential dependent profile of SHG was obtained for 1064 nm excitation (Figure 2d), the input light power should be at least 3 times larger than that for the 532 nm excitation measurement to obtain a reasonable signal/noise ratio. In addition, the minor difference between the SHG behaviors for each excitation wavelength was observed in the platinum oxide formation region.

Figure 3 shows (a) the cyclic voltammogram and (b) the potential dependence of the 1064 nm-excited SHG signal (532 nm) with \( E_{\text{ads}} = -0.2 \) V. In the first anodic scan (solid line), the current corresponding to the formation of upd-H was not found and two distinct CO oxidation peaks were observed at +0.2 and +0.38 V. The small peak around +0.2 V and the peak around +0.38 V are referred to as a prepeak and a main peak, respectively.⁵ It is well-known that the peak potential and the shapes of these peaks depend on pH, anion species, sweep rate, and \( E_{\text{ads}} \).⁵,¹⁹,⁶⁷,⁶⁸ The shape of the CV after the main peak is very similar to that from the bare Pt electrode (Figure 1a). The voltammogram for the second potential scan, represented by a dotted line, showed the hydrogen waves and no trace of the CO oxidation peaks. In the first anodic sweep, the SHG signal from the CO(a)/Pt surface (solid line) decreased monotonically as the potential was scanned from −0.2 V to more positive potentials and became almost the same value as that of the bare Pt electrode before the main oxidation peak of CO(a). The SHG response in the second scan was similar to that observed at the bare Pt electrode, represented by a broken line in Figure 2c. The SHG signal from the CO/Pt surface in the potential region more negative than +0.35 V was larger than that from the bare Pt surface in the double-layer region (+0.05 V to +0.4 V). The enhancement of the SHG signal from the CO-covered Pt electrode should not be due to upd-H, as no hydrogen waves were found in the voltammogram of the first anodic scan, apparently due to the existence of the CO(a) monolayer.
Figure 4 shows typical results of (a) the cyclic voltammogram and (b) the potential dependent profile of the 532 nm-excited SHG signal (266 nm) for the first two potential cycles after the preadsorption of CO for $E_{\text{ads}} = -0.2 \text{ V}$. While the voltammetric response was the same as that of Figure 3a as expected, the potential dependence of the SHG signal was different from that of the near-infrared excitation (Figure 3b). The SHG behavior seemed to correspond well to the features of the cyclic voltammogram in contrast to the results in Figure 3. The SHG signal was much higher than that of the bare Pt electrode in the double-layer region and was fairly constant in the potential region more negative than the main oxidation peak of CO(a). The SHG signal did not change with the prepeak. It decreased reversibly with the main oxidation peak of CO(a) in the first scan and became the same as that of the bare Pt electrode. Only the enhancement of the SHG with the formation of upd-H in the negative potential region was reversibly observed, and the potential dependence of the SHG signal after the second scan was almost identical to that in Figure 2. Essentially the same SHG behavior was observed by visible excitation in the wavelength range between 520 and 680 nm.

To confirm that the enhancement of the SHG signal with visible excitation is due to CO(a), the effect of $E_{\text{ads}}$ on the potential dependence of the SHG signal was investigated. In general, the potential where the oxidation of CO(a) occurs shifts positive with $E_{\text{ads}}$ being more positive. Figure 5 shows the potential dependence of (a) the current and (b) the 650 nm-excited SHG signal (325 nm) with $E_{\text{ads}} = -0.15 \text{ V}$ (solid line) and $E_{\text{ads}} = +0.15 \text{ V}$ (broken line). The essential features of these results were similar. The SHG signal was higher than that at the bare Pt electrode and was fairly constant in the potential region where the Pt surface was covered with CO. The SHG signal decreased as soon as CO(a) oxidation current flowed. The position of the main oxidation peak of the latter (+0.46 V) was a little positive of the former (+0.41 V), as expected, and correspondingly, the SHG signal started to decrease at the more negative potential in the former. Thus, it was concluded that the SHG signal at 650 nm excitation was enhanced by the existence of CO(a) that was oxidized at the main oxidation peak.

Figure 6 shows (a) the cyclic voltammogram and (b) the potential dependence of the 1064 nm- and 580 nm-excited SFG signals (375 nm) with $E_{\text{ads}} = -0.15 \text{ V}$. The SFG signal was fairly constant in the potential region more negative than the main oxidation peak of CO(a) in the first cycle. A large enhancement of the SFG signal by upd-H was apparent in the
of CO(a) on the Pt surface for all the excitation wavelengths in the UV region, than that by the existence of upd-H. The adsorption of CO(a) occurs was more localized, perhaps by the existence of CO(a) became more positive. These results suggest that these differences in the enhancement were caused by the difference in the NLO wavelengths of generated photons. Consequently, the energy range where the enhancement of nonlinear optical signal was higher at negative potential for near-infrared excitation, as already mentioned. Thus, the mechanism for the enhancement of the NLO signal should be different for each excitation wavelength.

Discussion

The SHG characteristics of CO(a) on Pt have been investigated in UHV. The exposure to CO induced a rather complex change of SHG signal at the Pt surface depending on the CO pressure in UHV. The 532 nm-excited SHG signal from a Pt surface first increased by the exposure of CO. After it reached the maximum, which is only ca. 120% of the SHG signal from the bare platinum surface, it started to decrease with the increase of the CO pressure. It increased again with further increase of the CO pressure. In contrast, the 532 nm-excited SHG signal from a Pt surface in the electrochemical environment. Thus, the mechanism for the enhancement of the SHG signal at the Pt surface depending on the CO pressure. In the case of SHG, \( \omega_1 = \omega_2 = \omega \), i.e., \( \omega_1 + \omega_2 = 2\omega \). Figure 7 shows the wavelength dependence of SHG at \(-0.15\) and \(+0.15\) V. Although \( f_{\text{CO}} \) is larger than unity in all the cases, the enhancement is more significant when visible light was employed for excitation. The most significant difference is, however, while \( f_{\text{CO}} \) was independent of the potential for visible excitation, \( f_{\text{CO}} \) was higher at negative potential for near-infrared excitation, as already mentioned. Thus, the mechanism for the enhancement of the NLO signal should be different for each excitation wavelength.

The General Treatment of the NLO Signal. The NLO light intensity arising from a metal surface has been treated in detail by several authors and is briefly described here. At a metal-solution interface, the induced surface nonlinear polar-
Figure 3). This result suggests that the enhancement is not due to the resonant enhancement by hydrogen absorption and is disturbed by oxide formation in the positive potential region. Adsorption of CO causes expansion of the potential windown, providing favorable circumstances to observe the EISHG effect.

**NLO Behaviors with Visible Excitation: Resonant Enhancement.** NLO enhancement with visible excitation was much higher than that with near-infrared excitation and depended on the amount of CO(a). If the nonresonant contribution is dominant for all the cases examined here, the wavelength dependence of the SHG must be small. The rather large wavelength dependence of the NLO response shown in Figure 7 suggests a relatively large contribution of the resonant NLO effect for the enhancement. The NLO enhancement in the resonance regime appears as a result of an energetic coupling between the photon associated with the NLO process and the electron transition. Since the resonant NLO enhancement can be observed when either the fundamental photon or the NLO photon is coupled with the electron transition, the determination of the resonant photon energy is difficult using SHG measurements with a single excitation wavelength.

Since the SHG enhancement at the 1064 nm-input/532 nm-output condition was nonresonant but the 532 nm-input/266 nm-output condition was resonant as described above, not visible photons but ultraviolet photons above 3.5 eV should be coupled with a transition. If visible photons are coupled with the transition, the SHG response at the 1064 nm-input/532 nm-output condition should be similar to that at the 532 nm-input/266 nm-output condition. The results of SFG presented in Figure 6 also support the resonance of the ultraviolet photon. Under 1064 and 580 nm excitations, the SFG signal (375 nm) was not enhanced by CO(a) as much as the SHG signal (290 nm). If the visible photon contributed to the resonance, the enhancement of 1064 nm- and 580 nm-excited SFG signals by CO(a) should be comparable to that of the SHG signal in Figure 4 and Figure 5.

Additional confirmation of the coupling in the UV region was given by studies with linear optics. An absorption peak around 270 nm (4.59 eV) was observed for the CO/Pt surface by potential-modulated reflectance spectroscopy (PMRS) and differential reflectance spectroscopy. This absorption was attributed to charge transfer transition of the CO--Pt surface complex, although a detailed description was not provided. The electronic structure of the CO/Pt surface complex was thus investigated with electron spectroscopic techniques in UHV environment. According to UV photoemission spectroscopy (UPS) studies, occupied states originating from 4σ and 5σ + 1π molecular states of CO are found to be positioned around 11.8 and 9.2 eV, respectively, below the Fermi energy (E_F). Inverse photoemission spectroscopy (IPS) studies showed that two unoccupied states are located at 1.5 and 4.5 eV above E_F, which are assigned to the antibonding 5σ, and 2π*, respectively. Fukutani et al. summarized these results and showed the energies of the CO/Pt system, but they did not mention any states related to CO(a) near the Fermi level. Schmidt et al. examined the electronic states near the Fermi level by measuring the potential dependence of the CO stretching vibration lifetime with time-resolved IR-visible sum frequency generation technique and showed a rough sketch of the density of 2π*-derived states. The energy diagram for the CO/Pt system is schematically shown in Figure 8, combining the results of refs 82–84.

As for the SHG enhancement, the lower transition threshold may be around 3.5 eV (see Figure 7). Most of the electronic transitions considered for the CO/Pt (111) surface, e.g., 5σ_b,
the (introduced by the modification of eq 5 into eq 6. Figure 9 shows
f, are ruled out as responsible for the resonance because photon
E

unoccupied states of Pt with adsorbed CO.

where

Energy diagram and assignments of occupied and unoccupied states of Pt with adsorbed CO.

\( \sigma^2 \) are the proportionality constants that are introduced by the modification of eq 5 into eq 6. Figure 9 shows the \( (I(2\omega)/I(2\omega)_{0})^{1/2} \) charge density \( (Q_{CO}) \) plot for the CO oxidation process presented in Figure 4, where \( \omega_1 = \omega_2 \). To calculate the charge density for CO oxidation, the double-layer charging current was subtracted assuming that the current in the double-layer region was independent of potential. The value of \( (I(2\omega)/I(2\omega)_{0})^{1/2} \) was calculated by using the SHG signal at +0.2 V of the second scan in Figure 3b as \( I(2\omega)_{0} \) with the assumption that \( I(2\omega)_{0} \) was independent of potential. The linear relation in Figure 9 shows that eq 6 is valid in this case and the change of the SHG signal reflected only the inherent resonance nature of the bonding between the surface and CO, and the additional terms such as the adsorbate–adsorbate interaction are negligible.

Figure 9. Plot of the square root of the normalized SHG signal (266 nm) against the electric charge density for the CO oxidation using eq 6. The solid line shows a linear least squares fit. The excitation wavelength was 532 nm.

Conclusion

The NLO responses of CO adsorbed on a Pt electrode surface were investigated with various excitation wavelengths. The NLO signal was enhanced by the adsorption of CO in all the cases, and the enhancement factor of the NLO signal by the adsorption of CO depended on the three-wave-mixing wavelength. Different enhancement mechanisms seemed to be applicable for visible and infrared excitation. At the infrared excitation, the SHG signal changed with potential, reflecting a change in the surface charge density. On the other hand, in the case of the visible excited SHG and near-infrared–visible–excited SFG measurements, resonant NLO enhancement coupled with the electronic transition from the \( E_{1} \) of Pt to \( 2\pi_{a}^{*} \) of CO-(a) was observed. These results demonstrated the usefulness of NLO measurement, particularly with wavelength variability for \textit{in situ} study of the molecular electronic structure at electrochemical interfaces.

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References and Notes
