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Surface-enhanced IR absorption on platinum nanoparticles: an application to real-time monitoring of electrocatalytic reactions

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Molecules adsorbed on Pt nanoparticles prepared on Si by a chemical deposition technique exhibit extremely strong IR absorption, which enables fast time-resolved IR monitoring of electrocatalytic reactions.

Surface-enhanced IR absorption (SEIRA) is a phenomenon that IR absorption of molecules adsorbed on metal nanoparticles is significantly enhanced than would be expected in the normal measurements without the metal.[1] SEIRA spectroscopy (SEIRAS) has been applied to *in situ* study of electrochemical interfaces very successfully.[1] A theoretical calculation predicts that SEIRA effect can be observed on most metals if the size and shape of particles and their proximity to each other are well tuned.[2] However, metals have been limited mainly to Au, Ag and Cu in previous SEIRA experiments. The use of Pt-group metals having higher catalytic activity than the coinage metals is desired for wider practical applications of SEIRAS.

Recently several groups investigated the IR spectrum of CO adsorbed on nanoparticles of Pt-group metals deposited electrochemically on glassy carbon or bulk Pt.[3–5] The sputtering technique was also employed in preparing Pt-nanoparticle films.[6] From a comparison with the spectra of CO adsorbed on smooth Pt surfaces, Lu *et al*.[3] and Bjerke *et al*.[4] reported that the absorption is 10–20 times enhanced on Pt nanoparticles. However, it should be noted that the peak intensities they observed on nanoparticles (0.001–0.038 abs.) are comparable to those observed on Pt single-crystal surfaces (0.004–0.02 abs.).[7–9] Furthermore, the observed absorption bands are asymmetric or bipolar.[3,4,6] Inversion of absorption peaks also takes place depending on the preparation conditions of the Pt film.[3–5] The distortion and inversion of bands arise mainly from physical origins[4,5,10] and hampers detailed interpretation of observed spectra. In this communication, we report that organic and inorganic species adsorbed on Pt nanoparticles prepared on Si by using a chemical (or electroless) deposition technique exhibit much stronger absorption than reported before, and further the band shape is nearly symmetric as observed on smooth Pt surfaces. We demonstrate that SEIRAS is very useful for mechanistic investigations of electrocatalytic reactions on Pt nanoparticles.

SEIRA measurements were carried out with the so-called Kretschmann configuration (internal reflection measurements with a prism/metal/solution geometry). The prism used was a Si hemicylinder and a Pt-nanoparticle film electrode was deposited on the reflecting flat plane of the prism by the following procedure. First, Pd was deposited on the Si substrate surface by contacting with 0.5% HF containing 1 mM $PdCl_2$ for 5 min to improve the adhesion of the Pt film to the substrate.[11] After rinsing with Milli-Q water, Pt was deposited subsequently on the Pd layer with a commercially available plating bath (LECTROLESS PT100, Electroplating Engineering of Japan)† at 50 °C for a desired period of time (typically 8 min).

The spectroelectrochemical cell was described previously.[12] The electrode potential was controlled and measured with a potentiostat *vs.* the reversible hydrogen electrode (RHE). The counter electrode was a Pt gauze. Spectra were recorded on a Bio-Rad FTS-60A/896 spectrometer equipped with a MCT detector and a homemade reflection accessory (incident angle of 70°, single reflection).[13] Spectra are shown in terms of absorbance units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflectivity of the electrode with and without adsorbates.

Chemically deposited Pt films were shiny as massive Pt, but scanning electron microscopy revealed that the films consist of Pt nanoparticles with an average dimension of 100 nm. The thickness of the deposited metal layer estimated by AFM was about 50 nm. No signals from the Si substrate and Pd underlayer were detected by Auger electron spectroscopy. Cyclic voltammograms for the chemically deposited Pt electrode measured in 0.5 M H_2SO_4 were identical to those for clean polycrystalline Pt electrodes. Hydrogen adsorption peaks observed between 0.05 and 0.4 V were integrated to evaluate the surface area of the electrode. By assuming 210 μC cm^{-2} for hydrogen adsorption, the roughness factor of the electrode was estimated to be about 7.

The SEIRA effect of the Pt electrodes was examined by using CO. A CO adlayer was established at 0.1 V by bubbling CO gas through the solution and then residual CO in the solution was purged with Ar gas. Coverage of CO was estimated to be about 0.85 with respect to the Pt surface atoms from the CO oxidation peak in a voltammogram. Typical SEIRA spectra measured at a constant potential of 0.1 V with p- and s-polarized radiations are shown in Fig. 1. A spectrum collected at the same potential after removing CO from the surface by oxidation at 1 V was used as the reference for each polarization. Absorption bands are observed only for p-polarization, which is consistent with previous SEIRA studies on Au and Ag.[1,14] The strong band at 2073 cm^{-1} and the weak band at 1875 cm^{-1} are assigned to CO molecules adsorbed at on-top site (linear CO) and at bridge site (bridge CO), respectively.[7–9] Differently from the spectra measured on electrochemically deposited and sputtered Pt films,[3–6] the linear CO band is nearly symmetric as is observed on smooth Pt electrodes.[7–9] The down-going bands at about 3500 and 1610 cm^{-1} are assigned to the stretching and bending modes, respectively, of water squeezed from the interface by the CO adsorption.[12] The sharp up-going OH stretching band at 3660 cm^{-1} indicates the presence of water molecules free from hydrogen bonding.[12] Since CO is hydrophobic and the sharp OH stretching band appeared at relatively high CO coverage,

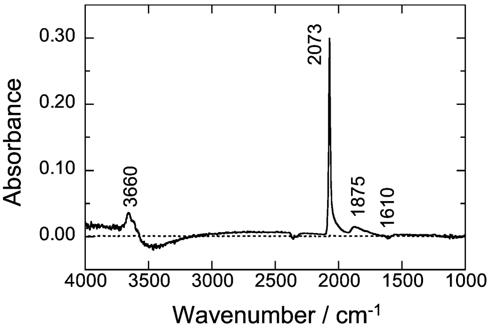

Fig. 1 SEIRA spectra of CO adsorbed on a chemically deposited Pt electrode in 0.5 M H_2SO_4 at 0.1 V for p (solid) and s (dotted) polarization.

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the water molecules are likely to be embedded in the CO adlayer.

It is worthwhile to note that the peak intensity of the linear CO band (0.3 abs.) is 15–75 times as large as that observed on smooth Pt electrodes with the reflection–absorption spectroscopy technique (0.004–0.02).[7–9] It is apparent that the larger surface area of the chemically deposited Pt film (*i.e.* a larger amount of CO adsorbed) contributes to the extremely strong absorption. However, even if the surface roughness is taken into account, the intensity is still 2–10 times larger on the chemically deposited Pt electrode. Comparison of the spectra measured with different optical configurations (internal and external reflection configurations) is not adequate to evaluate the enhancement factor. An theoretical calculation revealed that the enhancement factor exceeds 100.[15] Enhanced absorption was observed also for hydrogen atoms, HSO_4^- and many organic molecules.[15]

The high sensitivity of SEIRAS using the chemically deposited Pt nanoparticles is favorable for real-time monitoring of electrochemical reactions. As an example, Fig. 2 shows a series of 80 ms time-resolved spectra of a Pt electrode surface in 0.5 M H_2SO_4 containing 1 M formic acid, which were collected sequentially during a potential sweep from 0.1 to 1.3 and back to 0.1 V at a scan rate of 50 mV. The reference spectrum was collected at 0.1 V in the supporting electrolyte before adding formic acid. In addition to the linear and bridging CO bands, two peaks are identified at 1730 and 1325 cm^{-1}. These bands are assigned to the C=O stretching mode of formic acid in the solution and the symmetric COO stretchning mode of formate (HCOO) adsorbed on the Pt surface with a bridging configuration.[16] The formate band has not been reported in the literatute. The corresponding asymmetric COO stretching mode is missing in the spectra. On the basis of surface selection rule in SEIRAS,[1,14] the result implies that formate is oriented vertically or titlted facing the molecular plane toward the surface.

Electrooxidation of formic acid to CO_2 at Pt electrodes has received considerable interest in recent years as this is relevant to fuel cells.[17] It is generally accepted that formic acid is oxidezed *via* the so-called ‘dual-pathway mechanism’: a direct pathway in which formic acid is oxidized through short-lived reactive intermediates and an indirect pathway in which formic acid is decomposed to yield CO which is oxidized to CO_2.[17] The latter pathway is evidenced by the CO bands in the spectra. So far, several species such as Pt–C(=O)H and Pt–C(=O)OH have been speculated as the reactive intermediates in the direct pathway.[17] However, no species other than formate and CO were identifed in the present experiment. The integrated intensity of the formate band was nearly proportional to the oxidation current. When DCOOD was added into the solution after a HCOO adlayer had been established, the 1325 cm^{-1} band was found to decrease in intensity with time and a new band assignable to dueterated formate (DCOO) emerged at 1295 cm^{-1}. The H–D exchange reaction was not observed for H_2O–DCOOD and D_2O–HCOOH systems within the timescale of the experiment. Therefore, the observed H–D exhange can be interpreted by adsorbed formate readily decomposing to CO_2 and supplied continuously from the bulk solution. That is, the results strongly argue that formate is a reactive intermediate in the direct pathway of the formic acid oxidation.

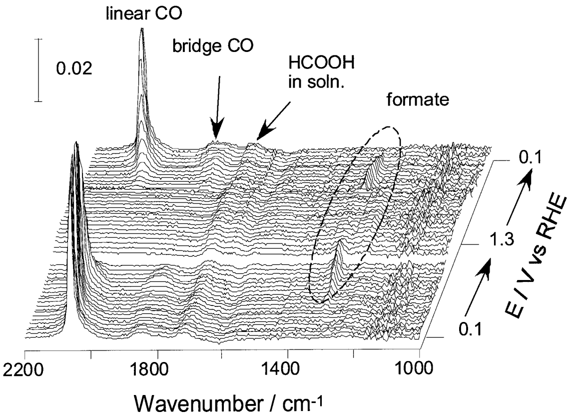

Fig. 2 Series of time-resolved SEIRA spectra of a Pt electrode in 0.5 M H_2SO_4 + 1 M HCOOH collected sequentially during a potential sweep from 0.1 to 1.3 and back to 0.1 V at a scan rate of 50 mV s^{-1}. The time-resolution used was 80 ms but spectra at every 0.8 s are shown for clarity. Unpolarized radiation was used.

As demonstrated, SEIRAS using chemically deposited Pt nanoparticles is very promissing for molecular scale analysis of electrocatalytic reactions. A mechanistic investigation of methanol electrooxidation on Pt electrodes directed toward the development of a direct methanol fuel cell is in progress.

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Notes and references

† Composition of the plating bath: 0.01 M hexaammineplatinum(IV) hydroxide + 0.06 M hydrazine monohydrate + 0.7–1.1 M ammonia + additives (stabilizer).

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