SNIFTIRS of CN⁻ at Au Electrode

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Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopic Study of Cyanide Ions at Gold Electrode

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The adsorption of cyanide ion on the gold electrode has been investigated by the subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS). The observations made by SNIFTIRS were consistent with those obtained by the polarization modulated Fourier transform infrared spectroscopy. According to the surface selection rule, cyanide ion appeared to adsorb on gold *via* either carbon or nitrogen lone pair electrons assuming a perpendicular orientation with respect to the metal surface. The possibility of presence of bridge-bound species seemed very infeasible. From the *ab initio* quantum mechanical calculation, adsorbate-to-metal bonding appeared to occur mainly *via* the 5σ donation from carbon to Au.

Introduction

The structure of the electrode/electrolyte interface plays an important role in electrochemistry and electrocatalysis.[1] The potential barrier arising from the distribution of charged and dipolar species in the double layer influences the rate of electrochemical reactions. Since majority of electrode reactions proceed through adsorbed intermediates, the electrocatalytic reactions are affected greatly by the nature of adsorbed species.

In the last decade, it has become possible to investigate the electrode/electrolyte interface at the molecular level in conjunction with electrochemical measurements. Among various physicochemical methods, reflection-absorption spectroscopy and surface-enhanced Raman scattering (SERS) have been regarded as the most suitable methods for *in situ* studies of electrode/electrolyte interface.[2-5] Although both the specular reflection in the UV-visible region and SERS are extremely sensitive, they suffer, respectively, drawbacks due to inability to identify adsorbed species and inapplicability to wide variety of metal electrodes. In contrast, specular reflectioin spectroscopy in the infrared range appears to be an ideal *in situ* method for the identification of molecules adsorbed at the electrode/electrolyte interface without limitation on the kind of metal electrodes.

Internal and external reflectance methods can be used as an *in situ* infrared technique. The former method operates in accordance with the principle of attenuated total reflection.[6] The latter method can be operated in various ways depending on the kinds of spectrometer.[7-11] With a dispersive spectrometer, *in situ* infrared spectroscopic studies have been performed by the techniques such as electrochemically modulated infrared reflectance spectroscopy (EMIRS), infrared reflection-absorption spectroscopy (IRRAS), and linear potential sweep infrared reflectance spectroscopy (LPSIRS). With a FT-IR spectrometer, similar studies have been performed by using the methods of polarization modulation FT-IR spectroscopy (PM-FTIRS) and subtractively normalized interfacial FT-IR spectroscopy (SNIFTIRS).

Adsorption of CN⁻ on silver and gold electrodes is of great interest because of its structural similarity to CO that can be used in fuel cells. Accordingly, its adsorption behavior
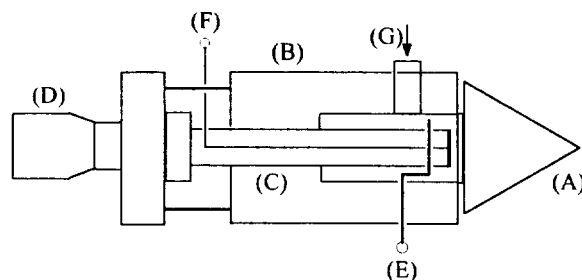

Figure 1. Schematic diagram of electrochemical cell used in SNIFTIRS.

(A) CaF₂ optical window, (B) Teflon cell body, (C) Working electrode, (D) Micrometer, (E) Platinum counter electrode, (F) Connection to working electrode, (G) Inlet hole for SCE.

has been investigated by SERS, EMIRS, and PM-FTIRS.[12-15] In this report, we present the spectra of CN⁻ adsorbed on a smooth gold electrode obtained by *in situ* SNIFTIRS. It is found that the potential dependence of adsorption behavior can be established more clearly from SNIFTIRS than from SERS, EMIRS and PM-FTIRS.

Experimental

The schematic diagram of electrochemical cell used is drawn in Figure 1. The cell body was made from Teflon and a triangular CaF₂ prism was used as an optical window. The polycrystalline gold (Aldrich, 99.99%) electrode attached to a cylindrical Teflon rod was initially polished with 0.3 and 0.05 μm γ-alumina successively, and then sonicated in distilled water before use. The angle of incidence of p-polarized light was *ca.* 70° with respect to the electrode surface normal. The infrared spectra were obtained with a Bruker IFS 113 v Fourier transform spectrometer equipped with a globar light source and a liquid N₂ cooled mercury cadmium telluride detector. A specular reflection attachment (Harrick VRA) was used in conjunction with a Harrick KRS-5 wire grid polarizer. The spectra were obtained by recording the reference and sample interferograms at two different potentials alternately after every 32 scans. The collection of interferograms was synchronized with the potential change such
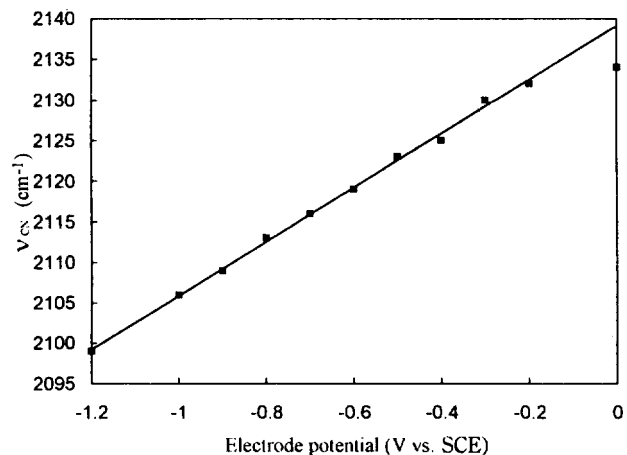
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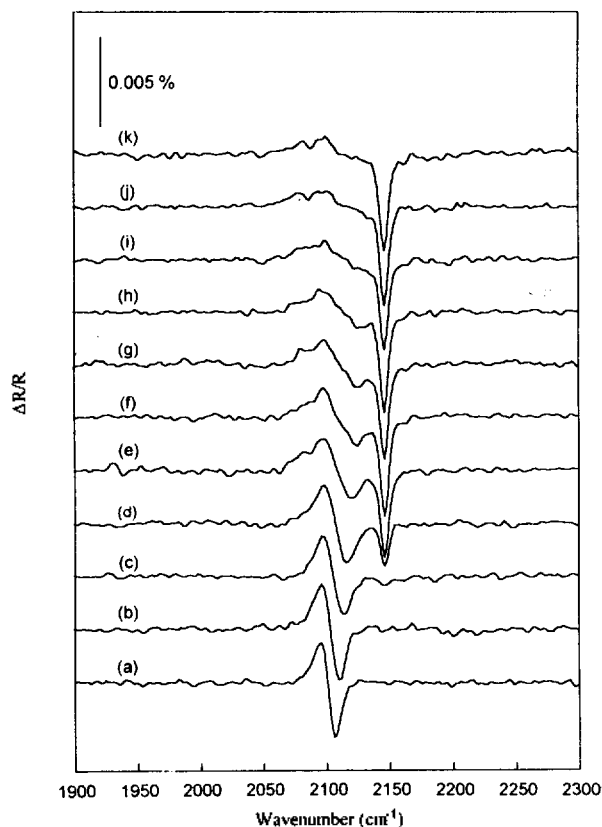
Figure 2. Surface-sensitive *in situ* PDIR spectra of 0.01 M KCN in 0.10 M NaClO$_4$ solution at a gold electrode obtained by SNIF-TIRS as a function of applied potential. The reference potential was -1.2 V *vs.* SCE. The sample potential was (a) -1.0 V, (b) -0.9 V, (c) -0.8 V, (d) -0.7 V, (e) -0.6 V, (f) -0.5 V, (g) -0.4 V, (h) -0.3 V, (i) -0.2 V, (j) 0 V, (k) 0.2 V for each spectrum.

Figure 3. Potential dependence of the band center position of the surface cyanide species on gold.

that the former to start at 4-5 seconds later after the later was made. The total scans at each specified potential were 1024 times with 4 cm^{-1} resolution. The Happ-Genzel apodization function was used in Fourier transforming the interferograms. The electrode potential was varied with respect to the saturated calomel electrode (SCE). The aqueous sample solution consisting of 0.01 M KCN and 0.1 M NaClO$_4$ was bubbled with N$_2$ gas before filling into the electrochemical cell. All the chemicals were reagent grade, and the triply distilled water (Barnstead Co. Nanopure II) was used throughout in the preparation of aqueous solutions.

Results and Discussion

Figure 2 shows the potential difference infrared (PDIR) spectra of CN$^-$ at gold electrode obtained in the potential range from -1.0 to 0.2 V using the SNIFTIRS method. When recording the PDIR spectra, the reference potential was set at -1.2 V. A single bipolar peak appears distinctly at near 2100 cm^{-1} in the potential range of -1.0 to -0.8 V. Referring to the principle of SNIFTIRS,[7] the positive peak has to be rendered to the chemical species existing at the reference potential, *i.e.*, -1.2 V, while the negative peak to those existing at the specified sampling potential. In fact, the posi-

tion of positive peak centered at 2096 cm^{-1} was observed barely to change with the potential variation. According to the cyclic voltammogram, any electrochemical reaction hardly occurs at around -1.0 V. Since the CN stretching mode of the cyanide ions in the aqueous phase appears usually at 2080 cm^{-1}, the positive peak can then be attributed to cyanide adsorbed on gold at -1.2 V. The negative peak centered at 2106 cm^{-1} at -1.0 V was found, on the other hand, to blue-shift as the applied potential was increased. Since the corresponding peak is not observable with s-polarized light, the peak is surely to arise from the adsorbed species. Referring once again that no electrochemical reaction takes place at near -1.0 V, the species can be attributed to surface cyanide species at the specified sampling potential. The present assignment agrees with that made from the earlier PM-FTIRS study.[14,15]

According to the infrared surface selection rule,[16,17] only the vibrational mode whose dipole moment derivative has a perpendicular component with respect to the metal surface can be exclusively excited by the specular reflection of p-polarized light. The appearance of ν(CN) band due to surface cyanide species dictates then that the bond axis of cyanide should assume a perpendicular stance with respect to the gold surface. This implies further that the adsorption does not occur *via* the C≡N π system. Nonetheless, it is not evident whether the surface bonding occurs *via* the nitrogen or *via* the carbon atom. At this moment, it would be worth to consider the degree of covalency of the metal-cyanide bond. If the adsorbate-metal bond is largely ionic, we would expect the band frequency of the adsorbed cyanide to increase when compared with the solution species as actually observed. In this case, binding through either carbon or nitrogen will be possible. On the other hand, if the adsorbate-metal bond is mainly covalent, one needs to consider both the 5σ donation from adsorbed cyanide to gold and the backdonation of 5d band of gold to the π* orbital of adsorbed cyanide. The 5σ orbital of cyanide has a slightly antibonding character and is contributed more by carbon atom than by nitrogen (vide infra). Hence, the 5σ donation will tend to increase the stretching frequency of adsorbed cyanide species but the backdonation enforces to decrease the frequency

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with respect to the free species in bulk. The fact that the CN stretching peak has blue-shifted by surface adsorption suggests then that the 5σ donation is more important than the metal-to-adsorbate backdonation. In this bonding scheme, cyanide should be considered to bind to gold *via* the carbon lone pair electrons.

In order to get further information on the binding scheme, *ab initio* quantum mechanical calculation has been performed by using the Gaussian 92 program for Windows.[18] Initially, the composition of 5σ orbital in CN⁻ was evaluated by using the 6−31＋G basis set. As mentioned above, the contribution of carbon AOs to the 5σ MO was much greater than that of nitrogen AOs; in the order of $C(2p_z)>C(3s)>N(2p_z)\cdots$. To examine the relative stability of two possible geometric isomers, Au-CN and Au-NC, single point energy calculations were repeated with a geometry optimization routine by varying the distances of C-N and Au-C or Au-N bonds. In this calculation, the LANL1DZ basis set was used, *i.e.* Dunning /Huzinaga valence double-zeta (DZ) for carbon and nitrogen atoms and Los Alamos ECP＋DZ for the gold atom. A bound state could be obtained for both isomers. For AuCN, the equilibrium distances of Au-C and C-N bonds were determined to be 2.0945 and 1.1613 Å, respectively, while for AuNC the distances of Au-N and N-C bonds were 2.1275 and 1.1799 Å, respectively. The AuCN species was calculated to be more stable than the AuNC species by 50 kJ/mol. This may suggest that cyanide ion should adsorb on the gold surface *via* the carbon lone pair electrons. Considering that the net charge of gold atom in AuCN is found to be 0.433 e, the interaction between the cyanide ion and the gold surface is conjectured to be more covalent than ionic.

The favorability of covalent interaction seems also inferable from the potential dependence of the CN stretching frequency of adsorbed cyanide species. Figure 3 displays the plots of the variation in the center position of negative peaks as a function of electrode potential, based on the spectra shown in Figure 2. It is interesting to notice that the band center shifts linearly with potential with a slope of 30 cm⁻¹ /V. A similar linear shift, *i.e. ca.* 30 cm⁻¹/V, has been reported for CN⁻ adsorbed on a silver electrode as well as for CO adsorbed on a platinum electrode.[14,19] In the PM-FTIRS study of CN⁻ at the gold electrode reported by Kunimatsu *et al.*[14,15], a similar peak shift was observed although their value was slightly larger than that measured in the present work. The CO molecule is known to bind to transition metal surfaces *via* the 5σ donation along with the metal-to-adsorbate π* backdonation.[20] Considering that CN⁻ and CO are isoelectronic and that the potential dependencies of CN⁻ stretching frequencies is much the same as that of CO stretching frequency on platinum, the bonding scheme for CN⁻ on gold could be regarded to be similar to that for CO on platinum although the mechanism of potential dependence of v(CO) is not still unequivocal.[20-24] Hence, it is concluded at this moment that cyanide adsorbs on the gold surface *via* its carbon atom.

It would be interesting to note that the adsorption behavior of CN⁻ onto gold and silver surfaces appears to be much different from that onto a palladium surface. From a SNIFTIRS study of CN⁻ at a palladium electrode, Ashley *et al.*[25] observed two peaks due to adsorbed cyanide species at 2065 and 1980 cm⁻¹ at 0.7 V. Those peaks assigned, res-

pectively, as linear and bridge-bound cyanide species red-shifted as the electrode potential was lowered. The peak positions of adsorbed species are substantially lower than that of free CN⁻ in bulk. Ashley *et al.* claimed thus that for Pd the metal-to-adsorbate π* backdonation should be favored over σ donation. For Au, we could not observe any peak attributable to a bridge-bound cyanide species. Considering that the bridge-bonding will be favorably to occur when the σ interaction is not as important as the π interaction, the 5d band of Au can be viewed unsuitable for backdonation.

As the potential of gold electrode was made more positive, anodic faradaic current increased substantially. Concurrently, a new peak began to appear distinctly at 2146 cm⁻¹ when the electrode potential reached up to −0.7 V (see Figure 2). Its peak position was hardly dependent on the applied potential. Its intensity increased, however, at the expense of the intensity of the potential dependent linearly adsorbed surface cyanide species as the potential was made more positive. The same observation was made by Kunimatsu *et al.*[14,15] from the PM-FTIRS experiment. Since the 2146 cm⁻¹ peak could be observable even with s-polarized light, the species responsible for the peak should be an anodic reaction product existing in the solution phase. As invoked by Kunimatsu *et al.*, the 2146 cm⁻¹ peak is attributed to Au(CN)₂⁻ complex ion in solution. The advantage of infrared reflection spectroscopy over SERS can be envisaged from the standpoint that in SERS the electrochemical reaction product like Au(CN)₂⁻ dissolved in the solution is difficult to be identified in comparison with the cases of SNIFTIRS and PM-FTIRS.

In summary, we have investigated the adsorption of CN⁻ on the gold electrode surface by SNIFTIRS. The observations made by SNIFTIRS were much the same as those from the earlier PM-FTIRS study. The cyanide ion was concluded to adsorb on the gold surface *via* the carbon lone pair electrons mainly by a covalent interaction. Although both the SNIFTIRS and PM-FTIRS methods could provide similar information, the former appeared to be more advantageous when one was interested in the comparative study at two different potentials in terms of the changes of adsorption behavior and the possible surface reactions.

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Syntheses of Morindaparvin A and Its Derivatives

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A general route for convergent syntheses of morindaparvin derivatives with 1,2-methylene-dioxyanthraquinone pattern is described. The anion of 2-methoxycyclohexanone (3), generated with lithium cyclohexylisopropylamine at −78℃, was sulfenylated with phenyl phenylthiosulfonate followed by elimination to afford α, β-unsaturated carbonyl system 8. 6-Methoxy-2-cyclohexen-1-one (8) was condensed with the four phthalide sulfones derivatives 10a-d, to provide morindaparvin derivatives, 1a-d.

Introduction

The rhizome and root of *Morinda Parvifolia* Bartl. (Rubiaceae) are well known as medicinal plants in Chinese folklore, and are used as herbal remedies for the treatment of bronchitis and whooping cough in humans.[1] From this plant, Chang and others have isolated and determined the structure of morindaparvin A & B which exhibit good biological activities[2] including antitumor activities. A number of morindaparvin analogs[3] with different substituents on the phenyl rings and its derivatives possessing an ethylenedioxy group at 1 to 4 position have been synthesized. Also, many other researchers[2,3] have discovered that morindaparvin contains potential antitumor properties. Based on this finding, it has been reported that not only morindaparvin with various kinds of substituents but also their derivatives[2,4] similar to 2, containing ethylenedioxy group at the positions 1 and 2, have been synthesized.
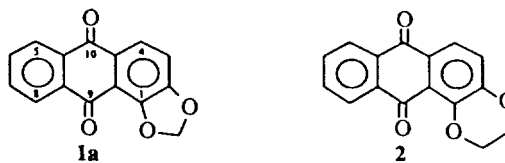
Morindaparvin A   1,2-Ethylenedioxyanthraquinone
(or 1,2-Methylenedioxyanthraquinone)

However, any derivatives with a hydroxyl group at either 5 or 8 position have not been synthesized. The hydroxyl group at either position will form an intramolecular hydrogen bonding with a carbonyl group in the quinone moiety, and consequently it may alter biological activity. To this end, we synthesized four morindaparvin derivatives 1a-d and would like to report the synthesis of theses compounds in this paper.