Electrochemistry of Hydroquinone Derivatives at Metal and Iodine-modified Metal Electrodes

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The difference in the electrochemical behavior of hydroquinone and pyrocatechol at platinum and gold surfaces was analyzed using voltammetry and attenuated total reflection Fourier transform infrared spectroscopy. The results show that the hydroquinone derivatives are adsorbed on a gold surface with vertical orientation, which makes the electron transfer between the bulk species and the electrode surface easier than that in the case of flat adsorption of hydroquinone derivatives that occurs at a platinum electrode. The formation of the vertical conformation and the rapid process of electron transfer were also confirmed by quantum chemistry calculations. In addition, the pre-adsorbed iodine on the electrodes played a key role on the adsorbed configuration and electron transfer of redox species.

Keywords Hydroquinone derivatives; Iodine-modified; Electrochemistry

Introduction

Platinum and gold surfaces can adsorb a wide variety of ions, atoms and molecular functional groups, which is often accompanied by oxidation-reduction or dissociation of them. Numerous previous works have made great progress in studying the surface chemistry of small organic molecules, especially electroactive molecules such as hydroquinone and catechol, etc., on a metal-liquid interface¹¹ for further understanding that at on solid-liquid interface. All the results indicate that the formation and orientation of the ordered adlayers of organic molecules on a solid-electrolyte interface play important roles in the electron transfer.

The surface properties of an adsorbed species are closely related to some factors, such as its pH value, its concentration¹², temperature¹³, the electrode potential¹⁴ and the surface atom orientation¹⁵,¹⁶. In particular, these factors may influence the adsorbate composition, orientation, molecular symmetry, conformation, electrochemical reactivity and chemical reaction pathways. Concerning the hydroquinone derivatives, Hubbard’s group¹⁷–²² has elucidated the structures of these adsorbates on a single crystal platinum surface, a polycrystalline platinum surface and a platinumized surface via many thin-layer electrochemistry (TLC) techniques, low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS) and infrared reflection-absorption spectroscopy (IRRAS). With the increase of the concentration of an adsorbate, a transition from horizontal orientation (at a concentration below 1 mmol/L) to vertical orientation (at a concentration above 1 mmol/L) on a platinum surface has been found. In addition, the surface roughness factor (RF) is a key factor in regulating adsorption orientation (when RF > 5, in general, flat orientation is much predominant). These results are helpful for exploring the relationship between electron transfer and adsorbate orientation. A further research in this respect, cannot only be used as a theoretical model of interfacial fabrication, but also contribute to the development of industrial applications of this technology, such as applications in adhesives, lubricants, batteries, fuel cells, electrocatalysis, electroplating processes and so on. Especial-
ly, a few modifiers containing hydroquinone groups have been introduced into chemically modified electrodes in previous works\textsuperscript{23-33}. Thus, the studies on the relationship between electron transfer and adsorbate orientation will be quite useful to elucidate such interfacial processes.

Although many redox species can be adsorbed on platinum and gold electrodes, a few of them will lose their redox properties, which will greatly change the dynamics of electron transfer. A few ions adsorbed specifically on an electrode surface can hinder the adsorption of other redox species in solution. Iodine was first used to modify platinum surfaces as early as 1955 by Lorez\textsuperscript{34}. Further studies by Osteryoung, Anson and their co-workers showed that the iodide species is adsorbed on a platinum surface as iodine atom~\textsuperscript{35-38}. The iodine-modified Pt surface has been extensively characterized by Hubbard and co-workers, with several surface analysis techniques, and also with electrochemistry\textsuperscript{39-43}. Itaya's group\textsuperscript{44-47} successfully reported the formation of highly ordered molecular adlayers at iodine-modified metal surfaces using scanning tunneling microscopy (STM).

In our work, iodine was also used to modify platinum and gold electrode surfaces, where it exhibits quite different electron transfer behavior. Here we report more detailed electrochemical, spectroscopic and quantum chemical investigations of the hydroquinone derivatives at platinum and gold electrodes. The effects of adsorbates' conformation and iodine modification upon electron transfer were further explored. It was also found that the vertically adsorbed species and iodine modification are advantageous to electron transfer. The IR measurements confirmed such an adsorbed structure described above, and the results of quantum chemical calculations provide further supports on this structure.

**Experimental**

1 **Chemicals and Solution**

Hydroquinone (crystalline, purity 99\%), catechol (crystalline, purity 99\%) and dihydroxynaphthalenes (crystalline, purity 98\%) were obtained from Aldrich Co. and used as received. Water used in solution preparation was purified in a Millipore system (>18 M\text{\Omega} \cdot \text{cm}). The supporting electrolyte was 1 mol/L H\textsubscript{2}SO\textsubscript{4} and was de-aerated with highly-pure nitrogen.

2 **Electrochemical Measurement**

Cyclic voltammetric measurement was performed with a CHI 660A electrochemical system (USA) in a conventional three-electrode cell. The platinum and gold disks (1 mm in diameter) were used as the working electrodes which were polished with 1.0, 0.3 and 0.05 \textmu m γ-Al\textsubscript{2}O\textsubscript{3} powder, respectively, and washed ultrasonically. All working electrodes used were scanned in a 1 mol/L H\textsubscript{2}SO\textsubscript{4} solution until stable cyclic voltammograms were obtained. A platinum wire was used as the counter electrode, and an Ag | AgCl (in saturated KCl solution) electrode as the reference electrode, against which all potentials were measured and reported. The disk working electrodes were electrochemically cleaned before each measurement until the same cyclic voltammograms were obtained.

The real area of the gold disk electrode was determined by the method described by Rodriguez \textit{et al.} via the chemisorption of iodine\textsuperscript{48}. The roughness factor of the gold electrode, given as the electrochemically determined area ($A = 2.4$ mm$^2$), divided by the geometric area, was about 3.0 for the electrode used. The real area of the platinum disk electrode ($A = 6.9$ mm$^2$) was attained by conventional measurement of the amount of adsorbed hydrogen. Its roughness factor was about 8.8. Iodine modification was performed by immersing the clean electrode into 0.5 mol/L KI/1 mol/L H\textsubscript{2}SO\textsubscript{4} for 5 min, and rinsing completely with a plenty of a 1 mol/L H\textsubscript{2}SO\textsubscript{4} solution.

3 **FTIR Characterization**

Attenuated total reflectance infrared (ATR-FTIR) spectra were obtained using a BIO-RAD FTS-7 (Digilab Division) spectrometer equipped with a liquid nitrogen cooled mercury-cadmium telluride (MCT) detector, a KRS-5 ATR element, and a gold wire-grid polarizer (Perkin Elmer). A spectral range from 4000 to 400 cm$^{-1}$, 256 scans, and an effective resolution of 2 cm$^{-1}$ were used. The polycrystalline platinum and gold films (with glass plates as substrate, size: 1 cm × 5 cm) used in the IR characterizations were prepared by physical vapor deposition (PVD) at a base pressure of 1.33 × 10$^{-5}$ Pa\textsuperscript{49} with a ca. 50 nm layer of chromium as the adhesion promoter. Flat terraces on the surfaces of these substrates were observed by using a scanning tunnelling microscope (STM). Such evaporated substrates were treated in a hot piranha solution\textsuperscript{50} prior to use, and thoroughly washed with copious water. Following this, the clean surfaces were rapidly immersed into the solutions of hydroquinone derivatives prepared freshly for ca. 5 min, completely washed with ultrapure water, and dried under highly-pure nitrogen\textsuperscript{22}.

4 **Quantum Chemistry Calculation**

The \textit{ab initio} SCF calculation described in Section 3 for Au/hydroquinone clusters was performed by using Gaussian 94 program. The 6$s$, 6$p$ and 5$d$ atomic orbit-
als of gold were treated by the basis set of \(10s, 5p,\) and \(3d\) primitive Gaussian-type orbitals contracted to \(2s, 1p\) and \(1d\) (10s5p3d/2s1p1d). The atomic orbitals of C, H, and O elements were expressed with an STO-3G basis set. The inner shells of gold atoms were described using effective core potentials (ECP-2)\(^{[51]}\), which replaced \([\text{Xe}]\) core. All the calculations were carried on a Crimson Workstation (SGI Co.).

**Results and Discussion**

1 Electrochemistry of Hydroquinone and Catechol at Bare and Iodine-modified Electrodes

The cyclic voltammetric curves were recorded to describe the effects of pre-adsorption, iodine modification, and electrode types on redox behavior of 0.9 mmol/L hydroquinone in 1 mol/L \(H_2SO_4\) [shown in Fig.1 (A) and (B)\(^{[1]}\)]. Fig. 1 (A) indicates that the pre-adsorbed hydroquinone on the platinum surface hinders the electron transfer (\(\Delta E = 153\) mV), but iodine modification avoids such hindrance (\(\Delta E = 56\) mV). It has been introduced extensively in previous reports that a clean Pt surface can spontaneously adsorb hydroquinone derivatives irreversibly from solution. When \(RF > 5\), the adsorbed orientation of hydroquinone on a platinum electrode is horizontal (\(\eta^6\)\(^{[10,20]}\) and the adsorption on a roughened surface occurs primarily in the flat orientation at all concentrations. In flat-adsorption, hydroquinone molecules lose hydrogen atoms of phenolic groups during chemisorption and form the horizontally oriented phenoxide, i.e., strong covalent organic-metal bonds form\(^{[9]}\):

\[
\text{OH} - \text{Pt Surface} \rightarrow \text{Pt} \quad \begin{array}{c}
\text{OH} \\
\text{Pt}
\end{array} + 2H^+ + 2e
\]

Since the redox reaction of a hydroquinone/quinone couple occurs only when the electroactive species is not attached directly to the electrode surface chemically, the formation of an adsorbed layer of phenoxide will affect electron transfer between a solution species and an electrode surface. Such an iodine modification might be effective for preventing hydroquinone adsorption from a platinum surface\(^{[40]}\), because no adsorption of hydroquinone on this modified layer has been found. Such a modification is advantageous to electron transfer between a solution species and an electrode interface. Over a large range of hydroquinone concentrations (0.1 mmol/L, 0.95 mmol/L, and 0.1 mol/L), all the results support such a conclusion.

Compared with that at a Pt electrode, the reversibility of hydroquinone adsorption at a pre-adsorption and iodine-modified Au electrode is extremely different [as shown in Fig.1 (B)\(^{[1]}\)]. A contradictory result seems to indicate that on a pre-adsorbed hydroquinone gold surface electron transfer is faster than on an iodine-modified Au surface (\(\Delta E = 36.5\) mV and \(\Delta E = 109\) mV, respectively). There are two possible reasons at least for such a delay occurring at an iodine-modified Au electrode: (1) a minute change of conductivity derived from iodine modification; (2) physisorption of solution species (hydroquinone) occurs on an iodine-modified gold surface (lots of researches have utilized the specific property and observed the morphology of a few molecules on the modified Au substrate by STM technology\(^{[48-47]}\)). Better redox reversibility of the hydroquinone adsorption occurring at a hydroquinone pre-adsorbed Au electrode than that at a platinum electrode can be possibly attributed to the formation of a specifically adsorbed configuration or orientation. Aromaticity and electroactivity of the phenolic groups will remain in such an adsorbed orientation, and electrons can easily transfer between solution species and an Au surface. The flat (\(\eta^6\)) and endwise (\(\eta^1\)) adsorption\(^{[10]}\) cannot sustain the aromaticity\(^{[21]}\) and electroactivity of adsorbed molecules, thus edgewise (\(\eta^7\)) orientation seems to be rational adsorbed pattern, which is shown as following:

Such a result can be easily reproduced in a large range of concentrations (2 \(\mu\)mol/L, 0.1 mmol/L, 0.95 mmol/L and 0.1 mol/L). With the increase of the hy-
droquinone concentration, on a smoothing platinum surface, the adsorbed orientation can undergo an irreversible transition from flat ($\eta^6$) to 2,3-edgewise ($\eta^2$) orientation, where the 2,3-edgewise ($\eta^2$) orientation at an Au electrode is predominant in a larger range of concentrations.

In previous works, it is considered that the adsorbed hydroquinone molecules with flat orientation is completely oxidized to CO$_2$ with $n_m$ being ca. 24 electrons per molecule$^{11}$, and the oxidation of the vertical entation, where the 2,3-edgewise ($\eta^2$) orientation at an Au electrode is predominant in a larger range of concentrations.

The slight deviation between $\sigma_{exp}$ and $\sigma_{calc}$ mainly derives from the invalid area that cannot be occupied by the adsorbed molecules (here are hydroquinone derivatives). Electrochemical behavior of pyrocatechol is similar to those of hydroquinone at platinum and gold electrodes (Fig. 2). On a platinum surface [Fig. 2 (A)], catechol oxidatively adsorbed impedes electron transfer ($\Delta E = 188$ mV) while an iodine-modified layer promotes the electron transfer between solution species and an electrode surface ($\Delta E = 40$ mV).

On a gold surface, the same opposite behavior can also be found, i.e., an iodine modification hinders the electron transfer [resulting in $\Delta E$ from 44 to 103 mV, Fig. 2 (B)] . On a gold surface, the same opposite CV behavior can also be found, i.e., an iodine modification hinders the electron transfer of pyrocatechol, and the pre-adsorbed pyrocatechol adlayer can promote the electron transfer [resulting in $\Delta E$ from 44 to 103 mV, Fig. 2 (B)]. The difference in electron transfer, as seen in CV measurements, should be ascribed to different adsorbed orientation of pyrocatechol on the gold substrate, as mentioned above in the case of hydroquinone. Also, the measurements of adsorbed amount and packing area are also listed in Table 1.

2 FTIR Characterizations of Adsorbed Hydroquinone at Platinum and Gold Electrodes

Image dipole effects on metallic surfaces restrict infrared activity of adsorbed molecule vibrations to those with dipole moments oscillating perpendicularly to the metal surface. Hence, the relative intensities of certain vibrations in a surface state, relative to those in a free state, provide a direct diagnosis standard of adsorbed molecule orientation. For a single molecular layer at self-supported metal substrates, the measure-

**Table 1 Adsorption data in 0.9 mmol/L hydroquinone/1 mol/L H$_2$SO$_4$ and 0.95 mmol/L pyrocatechol/1 mol/L H$_2$SO$_4$ at platinum and gold electrodes**

<table>
<thead>
<tr>
<th>Adsorbed molecule</th>
<th>Substrate</th>
<th>$n_m$ (Adsorbed orientation$^{[1,11]}$</th>
<th>$\Gamma_{exp}$/ (nm$^2$·cm$^{-2}$)</th>
<th>$\sigma_{exp}$/ (nm$^2$·molecule$^{-1}$)</th>
<th>$\sigma_{calc}$/ (nm$^2$·molecule$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>Platinum</td>
<td>24 ($\eta^6$)</td>
<td>0.259</td>
<td>0.64</td>
<td>0.538</td>
</tr>
<tr>
<td>Hydroquinone</td>
<td>Gold</td>
<td>12 ($\eta^2$)</td>
<td>0.424</td>
<td>0.391</td>
<td>0.286</td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td>Platinum</td>
<td>24 ($\eta^6$)</td>
<td>0.233</td>
<td>0.712</td>
<td>0.540</td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td>Gold</td>
<td>12 ($\eta^2$)</td>
<td>0.441</td>
<td>0.375</td>
<td>0.269</td>
</tr>
</tbody>
</table>

Fig. 2 Cyclic voltammograms of 0.95 mmol/L catechol in 1 mol/L H$_2$SO$_4$.

(A) At a bare (a) and an iodine-modified (b) Pt electrode; (B) at a bare (a) and an iodine-modified (b) Au electrode. Each voltammogram was recorded at 100 mV/s.
ments by means of polarized radiation, especially with p-polarized light, are essential because changes in substrate reflectivity due to adsorbate absorption can give orientation information [21, 52].

IR spectra of chemisorbed hydroquinone on polycrystalline gold and platinum surfaces are shown in Fig. 3 (A) and (B). In the measurement of Fig. 3(A), the parallelly polarized radiation was used. In a region of 2500-3300 cm\(^{-1}\), absorption bands of the adsorbed hydroquinone at an Au substrate exhibit similar shapes and positions to those of bulk hydroquinone \[^{[53]}\] , but for the absorbed hydroquinone on a Pt surface, no band can be obviously identified. According to the surface dipole selection rule\[^{[22, 52]}\] , the in-plane C-H and O-H (positions b and a) vibrations horizontally on Pt surface (\(\gamma^b\)) should not be IR active, and their polarized orientations are inconsistent with bond vibrational direction. However, in the case of vertical adsorption of hydroquinone at an Au substrate, the in-plane vibration is no longer parallel to the metal surface and, hence, IR activity of those two in-plane vibrations is shown. The displacement of O-H stretching vibration band from 3260 cm\(^{-1}\) of bulk hydroquinone to ca. 3180 cm\(^{-1}\) (position a) of vertically adsorbed hydroquinone may be related to the existence of intermolecularly ordered hydrogen bonds immobilized on Au surface.

With the polarized orientation transforming from parallel to perpendicular direction, obvious changes in the mid-infrared region also occur while on a flat adsorption Pt surface (data not shown here), hardly any change can be found in the IR spectra. Only a few weak bands related to the out-plane vibration (as 1435 cm\(^{-1}\), etc.) appear, which shows that there is little change in position and height peaks with the change in the polarized orientation manner. In the IR spectra of the adsorbed hydroquinone at the gold substrate, obvious changes can be seen as illustrated in Fig. 3 (B). Some bands (1730.1, 1697, 1691, 1648.5, 1642.3, 1633, 1570.8, 1555.1, 1518, 1490, 1454.4, 1433, 1417.1 cm\(^{-1}\)) gradually increase in intensity with augment of the perpendicular fraction. The bands assigned to the C=C stretching vibration of the aryl ring exhibit shifts due to bridging at the 2- and 3-positions with Pt atoms (1570.8, 1550, 1518, and 1490 cm\(^{-1}\)\[^{[2.54]}\] ). A few bands related to the C=O stretching vibration (1730.1, 1697, 1691, and 1648.5 cm\(^{-1}\) ) should be attributed to the easy oxidation of pre-adsorbed hydroquinone on such an adsorption surface, or the formation of a stably adsorbate conformation dependent on attraction with these oxidized quinone species.

3 Quantum Chemistry Analysis for Relationship Between Adsorbate Conformation and Electron Transfer

The adsorbing interactions and adsorption conformation between hydroquinone and Au (111) surface were investigated with \textit{ab initio} SCF. Fig. 4 shows the 18-atom cluster used to model the Au (111) surface. Considering the interaction between \(-\text{OH}\) groups of the adsorbed hydroquinone molecules and the second layer substrate atoms, two Au atoms were set below surface lattice. The positions of the Au atoms in the cluster model are fixed with a nearest-neighbor distance of 0.288 nm. In consistence with previous Hubbard’s works, an oxidized quinone (with two hydrogen atoms being eliminated) was used in this calculation.

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**Fig. 3** ATR-FTIR spectra of hydroquinone adsorbed on the gold and platinum surfaces by parallelly polarized radiation (A) and ATR-FTIR spectra of hydroquinone adsorbed on the gold surface (B) with the change of polarized orientation from parallel to perpendicular direction.

**Fig. 4** A front view of the 18-atom model of the Au (111) surface.
Two possible chemisorption modes are discussed. The first mode is the flat conformation, which is illustrated in Fig. 5(A). From an energy point of view, a flat conformation can hardly be formed. No any stable point can be found until the interacting distance is larger than 0.55 nm [Fig. 5(B)]. It indicates that the flat conformation is disadvantageous to constituting the chemical adsorption. The second mode is the vertical adsorption. It can form a stably adsorbed structure based on oxidation on the gold surface.

The relative model is presented in Fig. 6(A). Such an adsorption manner may result in molecular aggregates that are spontaneously formed with the formation of multiple hydrogen bonds between the hydroxyl groups with neighboring molecules. Therefore, a two-dimensional network forms due to the intermolecular interactions [Fig. 6(B)], which has not been dealt with in this work. Further work on these intermolecular interactions will be reported separately by the means of analysis of molecular mechanics.

4 Iodine Modification Effect on Electrochemistry of Dihydroxynaphthalene

As an example, the electrochemical behavior of 2,3-dihydroxynaphthalene was studied at bare and iodine-modified platinum electrodes [as shown in Fig. 7(A) and (B)]. The typical CV curves involved in specific adsorption were obtained. An irreversible oxidation process occurs at all the electrodes. Such results suggest that all reactants and their oxidized products can be adsorbed strongly on bare and iodine-modified surfaces. Fig. 7(C) shows a linear relationship of peak currents vs. scan rates, supporting a typically adsorbed process. On the CV curve of the iodine-modified sur-

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**Fig. 5** A front view of the flat adsorption of hydroquinone on Au(111) surface (A) and plot of relative total energy vs. distance between flat adsorbed quinone and Au(111) plane (B).

**Fig. 6** A front view of the vertical adsorption of hydroquinone on Au(111) surface (A) and pictorial representation of the possible network conformation based on multiple hydrogen bonds among the nearest-neighbor vertically adsorbed molecules (B).

**Fig. 7** Cyclic voltammogram of 5 mmol/L 2,3-dihydroxynaphthalene in 1 mol/L H₂SO₄ at a bare (100 mV/s) (A), an iodine-modified platinum electrode at different scan rates (a. 10, b. 25, c. 50, d. 75 and e. 100 mV/s) (B) and dependence of current peaks on scan rates at a bare platinum electrode (C).
face, a large forward peak shows that oxidized products are easier adsorbed specie than the reduced one, diphenol. The same results can also be obtained at the gold electrode.

References
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